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Abstract:

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Family: None

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PDF	Patent	Pub.Date	Inventor	Assignee	Title
	US6528033	2003-03-04	Barker; Jeremy	Valence Technology, Inc.	Method of making lithi containing materials

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(54) NONAQUEOUS ELECTROLYTE BATTERY

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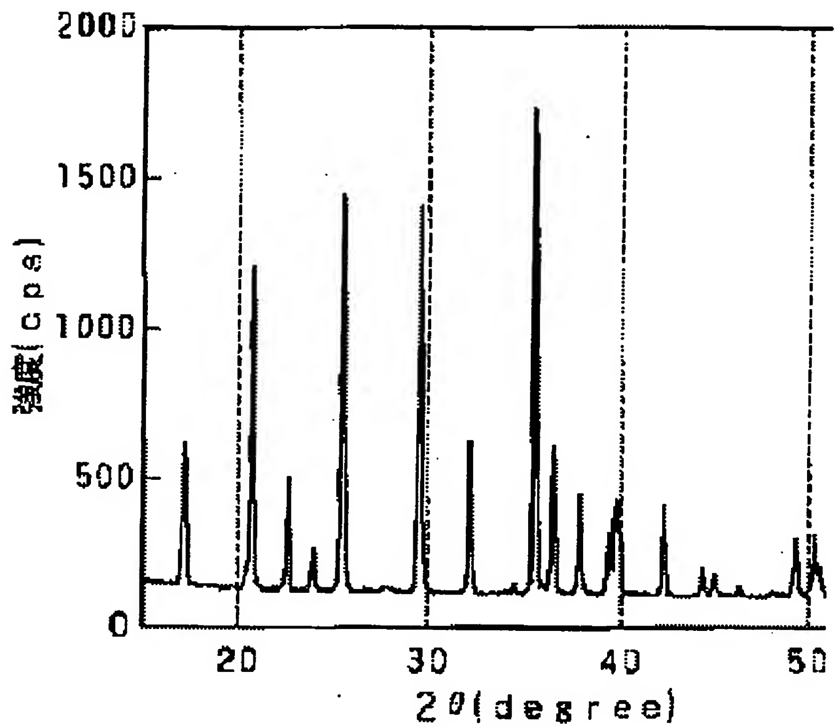

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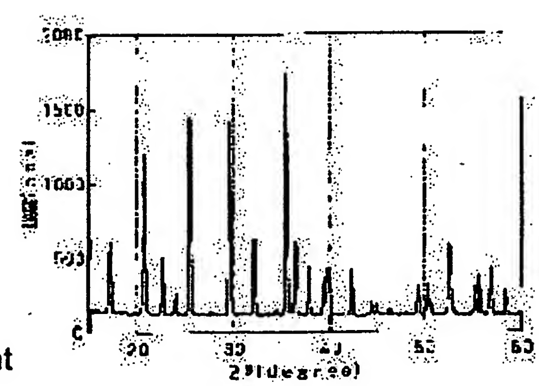

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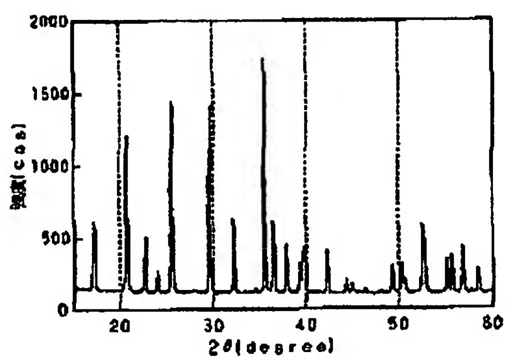
(54)【発明の名称】　非水電解質電池

(57)【要約】

【課題】　高容量化や低コスト化を実現しながら、環境対応性や安全性の問題を解決する。

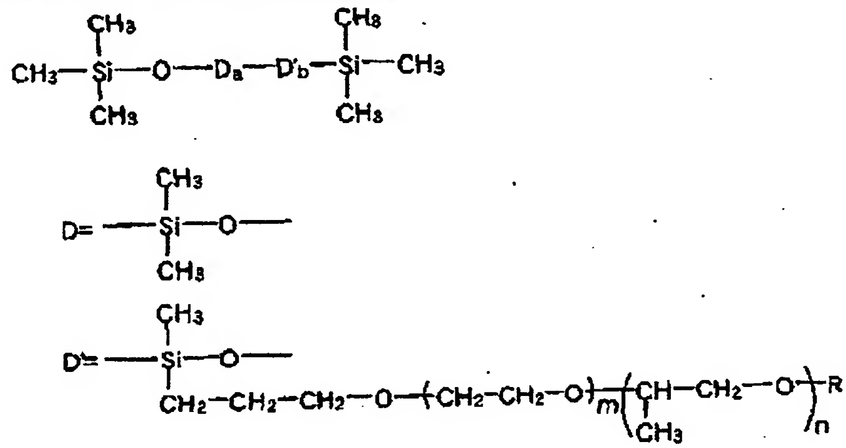
【解決手段】　リチウムを可逆的に吸蔵、放出する負極と、正極と、電解質とを備えた非水電解質電池が開示される。正極は、一般式$Li_xM_yPO_4$（ただし、式中、xは$0 \leqq x \leqq 2$、yは$0.8 \leqq y \leqq 1.2$である、また、Mは3d遷移金属を含む成分である。）で表される化合物を含有する。電解質は、シロキサン誘導体を含有する。正極に含まれる$Li_xM_yPO_4$は、粒子径が10μm以下のものを含むことが好ましい。また、正極に含まれる$Li_xM_yPO_4$は、10％体積累積径が1μm以下であることが好ましい。$Li_xM_yPO_4$としては、例えば$LiFePO_4$である



【特許請求の範囲】

【請求項１】 リチウムを可逆的に吸蔵，放出する負極と，一般式$Li_xM_yPO_4$（ただし、式中．xは０≦x≦２．yは０．８≦y≦１．２である，また、Mは３ｄ遷移金属を含む成分である。）で表される化合物を含有する正極と、電解質とを備え，上記電解質は．下記の化１で表されるシロキサン誘導体を含有することを特徴とする非水電解質電池。

【化１】



（式中、aは０から１００の整数を表し、bは１から１００の整数を表し、mは０から１００の整数を表し、nは０から１００の整数を表し、Rは水素原子又はアルキル基を表す。ただし、b＞１のときは、b個のD′は同じでも異なっていてもよい。D′及びRに含まれる水素原子はハロゲン原子で置き換えられていてもよい。）

【請求項２】 上記正極は．粒子径が１０μm以下の$Li_xM_yPO_4$を含むことを特徴とする請求項１記載の非水電解質電池。

【請求項３】 上記正極に含まれる$Li_xM_yPO_4$は、１０％体積累積径が１μm以下であることを特徴とする請求項１記載の非水電解質電池。

【請求項４】 上記$Li_xM_yPO_4$は．$LiFePO_4$であることを特徴とする請求項１記載の非水電解質電池。

【請求項５】 上記電解質は、互いに半相互侵入型高分子網目構造を形成することが可能な２種以上の高分子化合物を含み、これら高分子化合物のうちの１種が上記シロキサン誘導体であることを特徴とする請求項１記載の非水電解質電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は．秩序型オリビン構造を有する化合物を正極活物質とする非水電解質電池に関するものである。

【０００２】

【従来の技術】近年、種々の電子機器の飛躍的進歩とともに、長時間便利に、且つ経済的に使用できる電池として．再充電可能な二次電池の研究が進められている。代表的な二次電池としては．鉛蓄電池．アルカリ蓄電池、リチウム二次電池等が知られている。

【０００３】上記のような二次電池の中でも、特に、リチウム二次電池は、高出力．高エネルギー密度等の利点を有している。リチウム二次電池は．リチウムイオンを可逆的に吸蔵．放出可能な活物質を有する負極や正極と．非水電解質とから構成される。

【０００４】そして、一般に、リチウム二次電池の負極活物質としては．金属リチウム、リチウム合金．リチウムがドープされた導電性高分子、層状化合物（炭素材料や金属酸化物等）等が用いられている。

【０００５】また、正極活物質としては、金属酸化物、金属硫化物、あるいはポリマー等が用いられ、例えばTiS_2、MoS_2．$NbSe_2$、V_2O_5等の非含リチウム化合物や、$LiMO_2$（M＝Co、Ni、Mn．Fe等）のようなLiを含んだ複合酸化物が提案されている。

【０００６】

【発明が解決しようとする課題】ところで、上述のリチ

ウム二次電池においては、様々な課題が残されており、それらの改善が要望されている。

【0007】例えば、従来のリチウム二次電池においては、高エネルギー密度、高電圧が得られるとの観点から、対Li 4Vの電位を有する$LiCoO_2$が正極として広く実用化されている。$LiCoO_2$は、様々な面で理想的な正極材料であるが、Coは地球上に資源として偏在し、且つ稀少であるため、多大なコストを要し、また安定供給に問題があるといった問題があり、これに代わる正極材料の開発が望まれている。

【0008】正スピネル型構造を有する$LiMn_2O_4$（空間群Fd3m）は、現状では唯一の4V級のMnベースの正極材料であり、その容易な合成法、電池容量の点から非常に有望であり、既に一部実用化されている。

【0009】しかしながら、実電池への応用を考えた場合、高温保存時の容量劣化やMnの電解液中への溶解というような安定性に関する問題、さらにはサイクル特性に関する問題が未解決のまま残されている。

【0010】また、Mnよりも資源的に豊富で毒性に関してもCo、Ni、Mn等よりも遙かに低いFeをベースにした正極材料が実現できれば非常に有用であると考えられるが、これまでの検討では十分な特性は得られていない。これまでは、$LiCoO_2$や$LiNiO_2$と類似な構造を有する$LiFeO_2$を基本組成とする材料の検討が中心に行われてきたが、作製が困難な上に構造が不安定であり、2次電池用正極活物質としては全く不十分な特性しか実現されていない。

【0011】一方、電解液に関しても、従来、可燃性の有機溶媒が使用されており、様々な問題を残している。例えば、不用意な短絡時に急激に大電流が流れて発熱し、これによって電解液が気化、分解を起こし、ガスを発生するという問題がある。このようなガスの発生は、電池の破損や破裂等につながる可能性がある。

【0012】その解決方法としては、電池内圧の上昇により開裂する安全弁や電流遮断装置を設ける等の対処がなされている。

【0013】しかしながら、このような構造・機構の改良では、いかなる問題にも対処できるとは限らず、電池材料の抜本的な改善が必要になってきている。

【0014】そこで本発明は、かかる従来の実情に鑑みて提案されたものであり、高容量化や低コスト化を実現しながら、環境対応性や安全性の問題を低減することが可能な非水電解質電池を提供することを目的とする。

【0015】

【課題を解決するための手段】上述の目的を達成するために、本発明は、リチウムを可逆的に吸蔵、放出する負極と、一般式$Li_xM_yPO_4$（ただし、式中、xは$0 \leqq x \leqq 2$、yは$0.8 \leqq y \leqq 1.2$である。また、Mは3d遷移金属を含む成分である。）で表される化合物を含有する正極と、電解質とを備え、上記電解質は、シロキサン誘導体を含有することを特徴とするものである。

【0016】良く知られるように、FeはCo、Ni、Mn等の元素に比べると資源的に遙かに豊富であり、価格も安く、無毒無害である。さらに、シロキサン誘導体の主成分であるSiも地球上に極めて豊富に存在することも良く知られている。

【0017】したがって、$LiFePO_4$からなる正極材料とシロキサン誘導体を含有する電解質とを組み合わせることにより、低コストで環境負荷や毒性が極めて低い電気化学デバイスが実現される。

【0018】さらに、化学的安定性が高く、難燃性で且つ低蒸気圧の無機高分子であるシロキサンを電解質材料に用いることにより、電解液の気化、分解が抑制され、同時に電池の破損、発火の危険性も抑制され、優れた電池性能が達成される。

【0019】加えて、$LiFePO_4$の酸素はPと強固に共有結合しているため、解離が極めて起こり難く、燃焼反応を誘起し難いという特徴がある。したがって、上記シロキサン誘導体が有する難燃性、低蒸気圧という性質とも相俟って、極めて安全性の高い電池システムが構築される。

【0020】

【発明の実施の形態】以下、本発明を適用した非水電解質電池の構成について、図面を参照しながら詳細に説明する。

【0021】本発明の非水電解質電池は、基本的な構成要素として、正極、負極、電解質を備える。

【0022】そして、本発明においては、先ず、正極活物質としてオリビン構造を有する化合物、すなわち一般式$Li_xM_yPO_4$（ただし、式中、xは$0 \leqq x \leqq 2$、yは$0.8 \leqq y \leqq 1.2$である。また、Mは3d遷移金属を含む成分である。）で表される化合物を用いる。

【0023】$Li_xM_yPO_4$で表される化合物としては、例えば、$Li_xFe_yPO_4$、$Li_xMn_yPO_4$、$Li_xCo_yPO_4$、$Li_xNi_yPO_4$、$Li_xCu_yPO_4$、$Li_x(Fe,Mn)_yPO_4$、$Li_x(Fe,Co)_yPO_4$、$Li_x(Fe,Ni)_yPO_4$、$Li_x(Cu,Mn)_yPO_4$、$Li_x(Cu,Co)_yPO_4$、$Li_x(Cu,Ni)_yPO_4$等が挙げられる。なお、各化合物において、括弧内の元素の組成比は任意である。

【0024】例えば、$LiFePO_4$は、体積密度が3.6g/cm^3と大きく、3.4Vの高電位を発生し、理論容量も170mAh/gと大きい。しかも、$LiFePO_4$は、初期状態で、電気化学的に脱ドープ可能なLiを、Fe原子1個当たりに1個含んでいるので、リチウムイオン電池の正極活物質として能力が極めて高い。また、後述するように、この$LiFePO_4$は簡便な方法で合成することができる。

【0025】ただし、上記$LiFePO_4$を実際の電池

の正極活物質として用いようとした場合、これまでの合成法により得られる$LiFePO_4$では、60mAh／g～70mAh／g程度の実容量しか得られず、最大でも120mAh／g程度の実容量が実現されるに過ぎない。理論容量が170mAh／gであることを考えると、十分な容量が達成されているとは言い難い。

【0026】例えば、$LiFePO_4$と$LiMn_2O_4$とを比較した場合、$LiMn_2O_4$は、平均電圧が3.9Vであり、120mAh／gの容量を有し、さらに体積密度が4.2g／cm^{3}であるから、$LiFePO_4$は、$LiMn_2O_4$と比較して電圧、体積密度ともに1割程度小さいことになる。このため、同じ120mAh／gの容量を有する$LiFePO_4$は、$LiMn_2O_4$よりも重量エネルギー密度で1割以上、体積エネルギー密度で2割以上小さくなってしまう。

【0027】従って、$LiFePO_4$で$LiMn_2O_4$と同等レベルあるいはそれ以上のエネルギー密度を実現するためには、140mAh／gあるいはそれ以上の容量が要求されるが、$LiFePO_4$でこのような高容量はこれまで実現されていない。

【0028】また、$LiFePO_4$は、従来、合成原料となるFe源として酢酸鉄$Fe(CH_3COO)_2$等の2価の鉄の塩を用い、還元環境下にて800℃という比較的高温で加熱されることにより合成されている。合成時の加熱温度が高いと、その分エネルギーを消費することになり、また、反応装置等に与える負荷も大きい。

【0029】さらに、800℃という比較的高温で加熱されることにより合成された$LiFePO_4$は、結晶化が過剰に進行してしまう。このため、非水電解質電池の正極活物質に用いたとき、$LiFePO_4$粒子内でのリチウムの拡散が十分に起こらず、十分に高い容量を得ることができない虞れがある。

【0030】これらの問題を解消すべく、種々の検討を重ねた結果、$Li_xM_yPO_4$としては、粒子径が10μm以下であるものを含むものを用いるのが良いことがわかった。正極活物質が含有する$Li_xM_yPO_4$として、粒子径が10μm以下である$Li_xM_yPO_4$を含まない場合には、粒度分布が適切でないため、電荷担体であるリチウムが正極活物質の粒子内において十分に拡散することができないものと推測している。

【0031】また、$Li_xM_yPO_4$は、10%体積累積径が1μm以下であることが好ましい。10%体積累積径が1μmより大きい場合には、$Li_xM_yPO_4$は、結晶化が過度に進行し巨大粒子が大部分を占めてしまう虞れがある。このように結晶化が過度に進行すると、電荷担体であるリチウムが、正極活物質の粒子内において円滑に拡散することができない虞れがある。

【0032】上述のような粒度分布を有する$Li_xM_yPO_4$、例えば$LiFePO_4$は、以下に示すようにして合成する。

【0033】先ず、合成原料として例えば酢酸鉄（$Fe(CH_3COO)_2$）と、リン酸水素アンモニウム（$NH_4H_2PO_4$）と、炭酸リチウム（Li_2CO_3）とを所定比で混合して前駆体とする。ここで、合成原料の混合は十分に行う。合成原料を十分に混合することで、各原料が均一に混ざり合い、接触点が増えるため、従来よりも低い温度で$LiFePO_4$を合成することが可能になる。

【0034】次に、この前駆体を窒素等の不活性ガス雰囲気中、所定の温度で加熱することにより、$LiFePO_4$が合成される。

【0035】従来、$LiFePO_4$は例えば800℃という比較的高温で合成されていた。合成時の温度が高いと、その分エネルギーを消費することになり、また、反応装置等に与える負荷も大きかった。

【0036】そこで、合成原料を十分に混合して前駆体とし、窒素気流中で加熱して合成を行うことにより、例えば300℃という、従来の800℃に比べてはるかに低い温度で$LiFePO_4$を合成することが可能となる。すなわち、従来に比べてより広い温度範囲で$LiFePO_4$を合成することが可能となり、合成時の温度の選択の幅が広がる。

【0037】本発明者は、$LiFePO_4$を合成する際に、前駆体を加熱する温度（以下、合成温度と称する。）と、$LiFePO_4$を活物質として用いた電池の容量との関係に着目し、最適な$LiFePO_4$の合成温度について検討した。

【0038】その結果、$LiFePO_4$の合成温度は、400℃以上、700℃以下の範囲とすることが好ましいことがわかった。合成温度は400℃以上、600℃以下の範囲であることがより好ましい。

【0039】$LiFePO_4$の合成温度が400℃よりも低いと、化学反応と結晶化が十分に進まず、均一な$LiFePO_4$を得ることができない。また、$LiFePO_4$の合成温度が700℃よりも高いと、結晶化が過剰に進行してしまい、不純物の析出が抑えられない虞れがある。

【0040】なお、上述した製造方法において、前駆体を加熱合成する前に、前駆体に対して脱空気処理を施し、前駆体中に含まれる空気を予め除去しておくことが好ましい。

【0041】前駆体中に空気が残存していると、$LiFePO_4$の合成時に、2価の鉄化合物である酢酸鉄中のFe^{2+}が、空気中の酸素によって酸化されてFe^{3+}となってしまう。その結果、不純物である3価の鉄化合物が生成物の$LiFePO_4$中に混入してしまう。脱空気処理により予め前駆体中に含まれる空気を除去することで、酢酸鉄中のFe^{2+}の酸化を防ぐことができる。その結果、3価の鉄化合物が生成物の$LiFePO_4$中に混入せず、単相の$LiFePO_4$を得ることができる。

【００４２】$LiFePO_4$の合成原料としては、上述した化合物以外にも、水酸化リチウム、硝酸リチウム、酢酸リチウム、リン酸リチウム、リン酸第一鉄、酸化第一鉄等、種々の原料を用いることができるが、４００℃以上、７００℃以下という比較的低温で合成するためには、反応性の高い原料を用いることが好ましい。

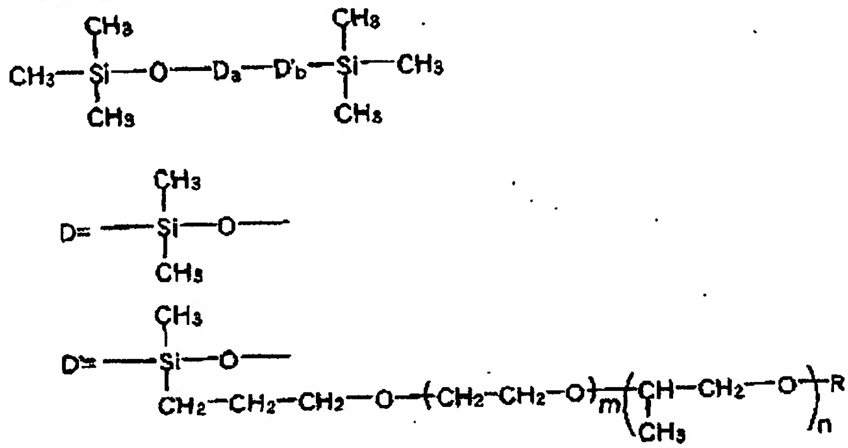
【００４３】上述したような製造方法では、合成原料を混合して前駆体とし、この前駆体を４００℃以上、７００℃以下の温度で加熱するので、化学反応と結晶化とが均一に進行し、且つ結晶化が過度に進行しない。これにより、不純物が無く、単相の$LiFePO_4$が得られる。このようにして合成される$LiFePO_4$を正極活物質として用いれば、$LiFePO_4$の理論容量である１７０ｍＡｈ／ｇに迫る高い実容量を実現することができる。

【００４４】なお、上記製造方法は、上述したような$LiFePO_4$に限らず、一般式$Li_xM_yPO_4$で表される化合物にも適用される。

【００４５】一方、本発明においては、電解質が下記の化２にて示されるシロキサン誘導体を含有する。

【００４６】

【化２】

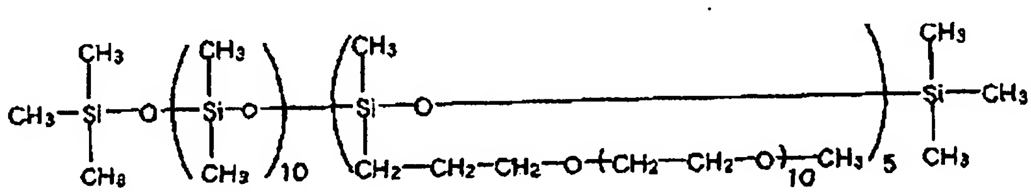


（式中、ａは０から１００の整数を表し、ｂは１から１００の整数を表し、ｍは０から１００の整数を表し、ｎは０から１００の整数を表し、Ｒは水素原子又はアルキル基を表す。ただし、ｂ＞１のときは、ｂ個のＤ′は同じでも異なっていてもよい。Ｄ′及びＲに含まれる水素原子はハロゲン原子で置き換えられていてもよい。）

【００４７】具体的には、下記の化３～化５に示すような構造を有するシロキサン誘導体を用いることができる。

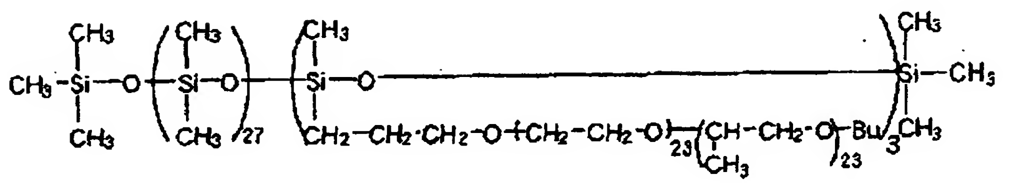
【００４８】

【化３】



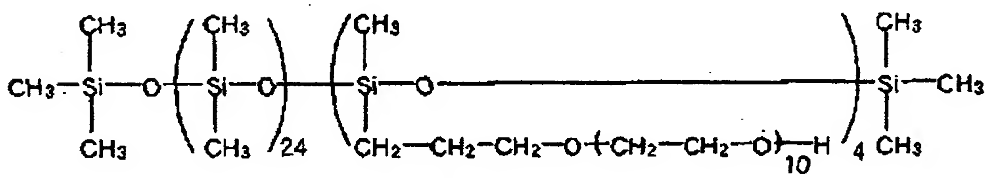
【００４９】

【化４】



（Bu= —CH₂—CH₂—CH₂—CH₃）

【００５０】 ＊ ＊【化５】



【００５１】上記シロキサン誘導体は、硅素と酸素の鎖状結合を基本骨格にもち、硅素に１価の有機基が側鎖として付加された鎖状型シロキサン誘導体であり、化学的安定性が高く、難燃性で低蒸気圧であるために熱化学的安定性にも優れる無機高分子である。

【００５２】電解質は、液状のいわゆる電解液であってもよいし、固体電解質やゲル状電解質であってもよい。

【００５３】電解質を電解液とする場合、シロキサン誘導体には、粘度が比較的低い溶液状であり、且つ軽金属塩を溶解し得る構造が求められる。すなわち、シロキサン誘導体は、温度２５℃における動粘性率が５０００ｃＳｔ（センチストークス）以下であり、平均分子量が１００００以下であることが求められる。

【００５４】さらに、電解液としては、温度２５℃における導電率が０．１ｍＳ・cm^{-1}以上であることがより好ましい。

【００５５】電解液として使用に耐え得る適正な粘度、混合に適する溶解性は、化２で示されるシロキサン誘導体におけるモノマーユニットＤ，Ｄ'の側鎖を適度に選択することにより可能となる。特に、モノマーユニットＤ'の側鎖は、エーテル結合を含むことが有利である。また、Ｄ，Ｄ'及び置換基Ｒ中の水素は、フッ素、ホウ素等のハロゲン元素で置き換えられていてもよい。

【００５６】電解液の非水溶媒としては、例えばプロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、ビニレンカーボネート、γ－ブチロラクトン、スルホラン、１，２－ジメトキシエタン、１，２－ジエトキシエタン、２－メチルテトラヒドロフラン、３－メチル１，３－ジオキソラン、プロピオン酸メチル、酪酸メチル、ジメチルカーボネート、ジエチルカーボネート、ジプロピルカーボネート等を使用することができる。特に、電圧安定性の点からは、プロピレンカーボネート、ビニレンカーボネート等の環状カーボネート類、ジメチルカーボネート、ジエチルカーボネート、ジプロピルカーボネート等の鎖状カーボネート類を使用することが好ましい。また、このような非水溶媒は、１種類を単独で用いてもよいし、２種類以上を混合して用いてもよい。

【００５７】固体電解質（溶媒を全く含まない完全固体電解質を含む。）やゲル電解質とする場合には、使用する高分子材料としては、シリコンゲル、アクリルゲル、アクリロニトリルゲル、ポリフォスファゼン変成ポリマー、ポリエチレンオキサイド、ポリプロピレンオキサイド、及びこれらの複合ポリマーや架橋ポリマー、変成ポリマー等、若しくはフッ素系ポリマーとして、例えばポリ（ビニリデンフルオロライド）やポリ（ビニリデンフルオロライド-co-ヘキサフルオロプロピレン）、ポリ（ビニリデンフルオロライド-co-テトラフルオロエチレン）、ポリ（ビニリデンフルオロライド-co-トリフルオロエチレン）等、及びこれらの混合物が各種使用できるが、勿論、これらに限定されるものではない。

【００５８】また、互いに半相互侵入型高分子網目構造を形成することが可能な２種以上の高分子化合物からなる組成物を固体電解質やゲル電解質のマトリクスポリマーとしてもよい。

【００５９】このうち少なくとも１種の高分子化合物は、化学的に架橋可能な官能基を有する化合物が当該架橋点において架橋された第１の高分子化合物であり、他の少なくとも１種の高分子化合物は、架橋可能な官能基を有さず軽金属塩を溶解する第２の高分子化合物、すな

わち上記シロキサン誘導体である。

【0060】この組成物は、第1の高分子化合物の3次元網目構造の基本骨格に、第2の高分子化合物であるシロキサン誘導体が相溶した状態になっている。

【0061】一般に、第1の高分子化合物は架橋されているので、機械的強度は強いが、架橋により分子運動が抑制され、溶存イオンの移動度が小さくなり、イオン伝導率は小さいという性質を有する。一方、第2の高分子化合物は、架橋されていないので、分子の運動量が高く、ガラス転移温度も低く、高いイオン伝導率を有するが、機械的強度に劣るという性質を有している。

【0062】ここでは、第1の高分子化合物と第2の高分子化合物とが半相互侵入型高分子網目構造を形成しており、それらの利点（強い機械的強度と高いイオン導電率）がそれぞれ生かされる。すなわち、半相互侵入型高分子網目構造においては、第1の高分子化合物と第2の高分子化合物との間では化学結合が実質的に生じておらず、第2の高分子化合物の分子運動が抑制されることはない。また、第2の高分子化合物の結晶化が起こり難くなるという相乗効果も加わり、広い温度範囲で各高分子化合物単独の場合よりも高いイオン導電率が得られる。さらに、第1の高分子化合物が構成する3次元網目構造により強い機械的強度が得られる。

【0063】架橋による3次元網目構造としては、直鎖状の化合物、あるいは分岐状の化合物の両末端、片末端を架橋したもの、側鎖に架橋点を有する化合物を架橋したもの等、任意である。

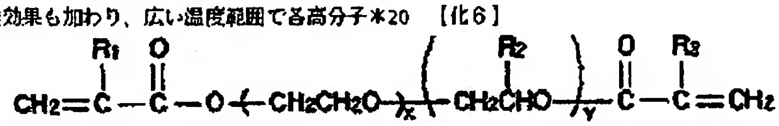
【0064】ただし、上記の3次元網目構造において、より高いイオン伝導率を実現するためには、ポリオキシアルキレンの分岐構造のようなエーテル結合を含む自由末端側鎖を有していることが好ましい。

【0065】第1の高分子化合物の架橋構造としては、エーテル結合、エステル結合、ウレタン結合等が挙げられるが、勿論これに限らず用途等に応じて任意の架橋構造を採用することができる。

【0066】このような第1の高分子化合物の具体例としては、下記の化6に示すジエステル化合物の重合体を挙げることができる。

【0067】

【化6】

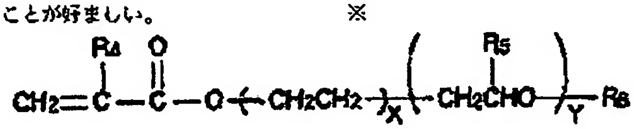


（式中、R_1、R_2およびR_3は水素原子または炭素数1～6のアルキル基を示し、それぞれは同一であっても異なっていてもよい。また、x≧1かつy≧0またはx≧0かつy≧1である。）

【0068】この場合、上述したような自由末端側鎖を導入することを目的に、下記の化7に示すモノエステル化合物を併用することが好ましい。

【0069】

【化7】



（式中、R_4、R_5およびR_6は水素原子または炭素数1～6のアルキル基を示し、それぞれは同一であっても異なっていてもよい。また、X≧1かつY≧0またはX≧0かつY≧1である。）

【0070】そのときのジエステル化合物とモノエステル化合物の比率（モノエステル化合物／ジエステル化合物）は、重量比で5．0以下とすることが好ましい。

【0071】上記電解質に溶解（相溶）させる軽金属塩には、リチウム、ナトリウム、アルミニウム等の軽金属の塩を使用することができ、電池の種類に応じて便宜定めることができる。

【0072】例えば、リチウム若しくはリチウムイオン二次電池を構成する場合には、$LiBF_4$、$LiClO_4$、$LiPF_6$、$LiAsF_6$、CF_3SO_3Li、$(CF_3SO_2)_2NLi$、$C_4F_9SO_3Li$、CF_3CO_2Li、$(CF_3CO_2)_2NLi$、$C_6F_5SO_3Li$、$C_8F_{17}SO_3Li$、$(C_2F_5SO_2)_2NLi$、$(C_4F_9SO_2)(CF_3SO_2)NLi$、$(FSO_2C_6F_4)(CF_3SO_2)NLi$、$((CF_3)_2CHOSO_2)_2NLi$、$(CF_3SO_2)_3CLi$、$(C_6F_3(CF_3)_2-3,5)_4BLi$、$LiCF_3$、$LiAlCl_4$等のリチウム塩を使用することができる。

【0073】非水電解質電池は、上記正極、電解質の他、負極等の構成要素を備えるが、他の構成要素は従来のものと同様のものを用いることができる。

【0074】以下、ボタン型の電池を例にして、非水電解質電池の構成要素について説明する。

【0075】ボタン型の非水電解質電池1は、図1に示すように、負極2と、負極2を収容する負極缶3と、正極4と、正極4を収容する正極缶5と、正極4と負極2との間に配されたセパレータ6と、絶縁ガスケット7とを備え、電解質として電解液を用いる場合には、負極缶

3及び正極缶5内に非水電解液が充填されてなる。固体電解質やゲル電解質を用いる場合には、固体電解質層、ゲル電解質層を負極2や正極4の活物質層上に形成する。

【0076】負極2は、負極集電体上に、負極活物質を含有する負極活物質層が形成されてなる。負極集電体としては、例えばニッケル箔等が用いられる。

【0077】負極活物質としては、リチウムをドープ／脱ドープ可能なものを用い、具体的には、金属リチウム、リチウム合金、リチウムがドープされた導電性高分子、層状化合物（炭素材料や金属酸化物など）等を用いる。

【0078】負極活物質層に含有される結合剤としては、この種の非水電解質電池の負極活物質層の結合剤として通常用いられている公知の樹脂材料等を用いることができる。負極活物質として例えば金属リチウム箔を用いた場合には、上記結合剤は不要である。

【0079】負極缶3は、負極2を収容するものであり、また、非水電解質電池1の外部端子（負極）となる。

【0080】正極4は、正極集電体上に、先に説明した$Li_xM_yPO_4$（例えば$LiFePO_4$）を正極活物質として含有する正極活物質層が形成されてなる。

【0081】正極集電体としては、例えばアルミニウム箔等が用いられる。

【0082】正極活物質層に含有される結合剤としては、この種の非水電解質電池の正極活物質層の結合剤として通常用いられている公知の樹脂材料等を用いることができる。

【0083】正極缶5は、正極4を収容するものであり、やはり非水電解質電池1の外部端子（正極）となる。

【0084】セパレータ6は、正極4と、負極2とを離間させるものであり、この種の非水電解質電池のセパレータとして通常用いられている公知の材料を用いることができ、例えばポリプロピレンなどの高分子フィルムが用いられる。また、リチウムイオン伝導度とエネルギー密度との関係から、セパレータの厚みはできるだけ薄いことが必要である。具体的には、セパレータの厚みは例えば50μm以下が好ましい。なお、電解質として固体電解質、ゲル電解質を用いた場合には、このセパレータ6は必ずしも設けなくともよい。

【0085】絶縁ガスケット7は、負極缶3に組み込まれ一体化されている。この絶縁ガスケット7は、負極缶3及び正極缶5内に充填された非水電解液の漏出を防止するためのものである。

【0086】本発明に係る非水電解質電池は、一次電池であってもよいし、二次電池であってもよい。また、円筒型、角型、コイン型、ボタン型等、その形状については特に限定されることはなく、薄型、大型等、任意のサイズとすることができる。

【0087】

【実施例】以下、本発明の非水電解質電池について、具体的な実験結果に基づいて説明する。

【0088】ここでは、オリビン型$LiFePO_4$を正極活物質とする非水電解質二次電池を作製した。

【0089】$LiFePO_4$を合成するには、先ず、結晶子サイズの大きい原料のリン酸二水素アンモニウム（$NH_4H_2PO_4$）を予め十分に粉砕した。次に、酢酸鉄（$Fe(CH_3COO)_2$）と、リン酸二水素アンモニウム（$NH_4H_2PO_4$）と、炭酸リチウム（Li_2CO_3）とを、モル比が2：2：1になるように十分に混合して前駆体とした。

【0090】次に、窒素雰囲気下、前駆体を320℃で12時間の仮焼きを行った後、窒素雰囲気下、前駆体を550℃で24時間加熱することにより$LiFePO_4$を合成した。

【0091】上述したような方法により合成された$LiFePO_4$について、粉末X線回折パターンを測定した。粉末X線回折の測定条件は下記の通りである。

【0092】

使用装置：リガクRINT2500回転対陰極
X線：CuKα、40kV、100mA
ゴニオメータ：縦型標準、半径185mm
カウンタモノクロメータ：使用
フィルタ：使用しない
スリット幅：
ダイバージェントスリット（DS）＝1°
レシービングスリット（RS）＝1°
スキャッタリングスリット（SS）＝1．5mm
計数装置：シンチレーションカウンタ
測定法：反射法、連続スキャン
走査範囲：2θ＝10°～80°
スキャンスピード：4°／分

測定された粉末X線パターンを図2に示す。合成された$LiFePO_4$においては、生成物中に$LiFePO_4$以外の不純物の存在は確認されず、単相の$LiFePO_4$が得られていることがわかる。

【0093】そこで次に、上述のようにして得られた$LiFePO_4$を正極活物質として用いて電池を作製した。

【0094】先ず、正極活物質（乾燥した$LiFePO_4$）70重量％と、導電剤（アセチレンブラック）25重量％と、結着剤（ポリフッ化ビニリデン）5重量％とを秤取し、これを溶媒（ジメチルホルムアミド）中に投入して均一に混合し、ペースト状の正極合剤を調製した。なお、ポリフッ化ビニリデンには、アルドリッチ社製の#1300を用いた。

【0095】次に、この正極合剤を集電体となるアルミニウムメッシュ上に塗布し、乾燥アルゴン雰囲気下、1

００℃で１時間乾燥して正極活物質層を形成した。

【００９６】そして、正極活物質層が形成されたアルミニウムメッシュを、直径１５ｍｍの円板状に打ち抜くことによりペレット状の正極とした。なお、この正極１個には６０ｍｇの活物質が担持されている。

【００９７】次に、リチウム金属箔を正極と略同形に打ち抜くことにより負極とした。

【００９８】次いで、シロキサン１ｋｇに対して１モルのＬｉＮ（CF_3SO_2）２を溶解させることにより非水電解液を調製した。

【００９９】以上のようにして得られた正極を正極缶に収容し、負極を負極缶に収容し、正極と負極との間にセパレータを配した。正極缶及び負極缶内に非水電解液を注入し、正極缶と負極缶とをかしめて固定することにより、２０２５型のコイン型テストセルを作製した。

【０１００】このテストセルについて、充放電試験を行った。テストセルに対して４．０Ｖまでの定電流充電を行った後、放電を行い、電池電圧が２．５Ｖまで低下した時点を放電終了とした。なお、充電、放電ともに常温（２３℃）で行い、充電、放電ともに電流密度は０．１＊２ｍＡ／cm^2とした。

【０１０１】充放電特性を図３に示す。図３より、本実施例のテストセルは良好な充放電特性を有することがわかる。

【０１０２】

【発明の効果】以上の説明からも明らかなように、本発明によれば、電池特性、経済性、環境対応性、安全性の全てにおいて優れた非水電解質電池を実現することができ、実用上の利点は大きい。

【０１０３】また、本発明の非水電解質電池は、従来のリチウムイオン電池よりも電圧が低めに設定されるため、ＩＣ等の駆動電圧の低下にも対応することができる。

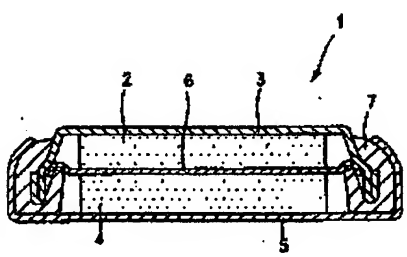
【図面の簡単な説明】

【図１】非水電解質電池の一構成例を示す概略断面図である。

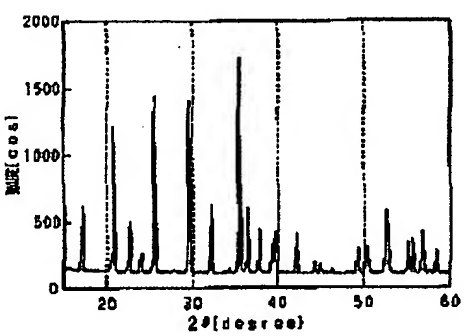
【図２】合成されたＬｉＦｅＰO_4の粉末Ｘ線回折パターンを示す図である。

【図３】作製されたテストセルの充放電特性を示す特性図である。

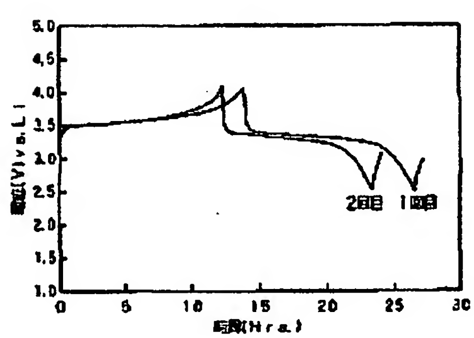
【図１】



【図２】



【図３】



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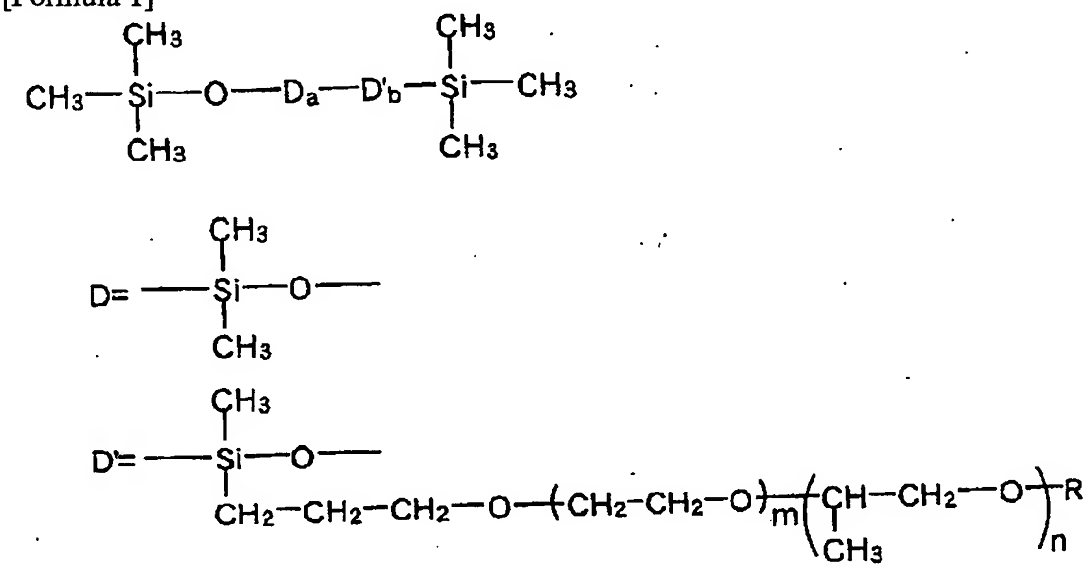
5H024 AA12 CC03 FF11 FF15 FF16 FF17 FF18 FF21 FF32 FF38 GG01
5H029 AJ07 AJ12 AK03 AK05 AK16 AL02 AL06 AL12 AL16 AM02 AM03 AM04 AM05 AM07 AM16 BJ03 BJ12 DJ17 EJ03 HJ02 HJ05

CLAIMS

[Claim(s)]

[Claim 1] It is [occlusion, the negative electrode to emit, and] a general formula LixMyPO4 (however, 0<=x<=2 and y of x are 0.8<=y<=1.2 among a formula.) in reversible about a lithium. Moreover, M is a component containing 3d transition metals. It is the nonaqueous electrolyte cell which is equipped with the positive electrode containing the compound expressed, and an electrolyte, and is characterized by the above-mentioned electrolyte containing the siloxane derivative expressed with following ** 1.

[Formula 1]



（式中、ａは０から１００の整数を表し、ｂは１から１００の整数を表し、ｍは０から１００の整数を表し、ｎは０から１００の整数を表し、Ｒは水素原子又はアルキル基を表す。ただし、ｂ＞１のときは、ｂ個のＤ′は同じでも異なっていてもよい。Ｄ′及びＲに含まれる水素原子はハロゲン原子で置き換えられていてもよい。）

[Claim 2] For the above-mentioned positive electrode, a particle diameter is LixMyPO4 10 micrometers or less. Nonaqueous electrolyte cell according to claim 1 characterized by containing.

[Claim 3] LixMyPO4 contained in the above-mentioned positive electrode Nonaqueous electrolyte cell according to claim 1 characterized by the diameter of volume accumulation being 1 micrometer or less 10%.

[Claim 4] the above LixMyPO4 LiFePO4 it is -- nonaqueous electrolyte cell according to claim 1 characterized by things

[Claim 5] The above-mentioned electrolyte is a nonaqueous electrolyte cell according to claim 1

characterized by one sort in these high molecular compounds being the above-mentioned siloxane derivative including two or more sorts of high molecular compounds which can form both the half-invasion type macromolecule network structure mutually.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the nonaqueous electrolyte cell which makes the compound which has order type olivine structure a positive active material.
[0002]
[Description of the Prior Art] In recent years, research of the rechargeable battery in which a recharge is possible is advanced as a cell which can be used conveniently [for a long time] and economically with fast progress of various electronic equipment. As a typical rechargeable battery, the lead accumulator, the alkaline battery, the lithium secondary battery, etc. are known.
[0003] Also in the above rechargeable batteries, especially the lithium secondary battery has advantages, such as high power and high-energy density. A lithium secondary battery consists of occlusion, the negative electrode and positive electrode which have the active material which can be emitted, and nonaqueous electrolyte in reversible in a lithium ion.
[0004] And generally as a negative-electrode active material of a lithium secondary battery, a conductive polymer, stratified compounds, etc. (carbon-material metallurgy group oxide etc.) with which the metal lithium, the lithium alloy, and the lithium were doped are used.
[0005] moreover, as a positive active material, a metallic oxide, metallic sulfide, or polymer uses -- having -- Ti_2S, MoS_2 and $NbSe_2$, and V_2O_5 etc. -- the non-** lithium compound and the multiple oxide containing Li like Li_xMO_2 (M=Co, nickel, Mn, Fe, etc.) are proposed [for example,]
[0006]
[Problem(s) to be Solved by the Invention] By the way, in the above-mentioned lithium secondary battery, various technical problems are left behind and those improvements are demanded.
[0007] For example, $LiCoO_2$ which has the potential of pair Li4V from a viewpoint that high-energy density and the high voltage are obtained in the conventional lithium secondary battery It is widely put in practical use as a positive electrode. $LiCoO_2$ In respect of being various, although it is an ideal positive-electrode material, Co is unevenly distributed as resources on the earth, and since it is rare, it requires great cost, and it has the problem that a problem is in adequate supply, and development of the positive-electrode material replaced with this is desired.
[0008] In the present condition, $LiMn_2O_4$ (space group Fd3m) which has normal-spinel type structure is the positive-electrode material of the 4V class only Mn base, from the point of the easy synthesis method and cell capacity, is very promising and is already put in practical use in part.
[0009] However, when the application to a real cell is considered, it is left behind while the problem about stability, such as capacity degradation at the time of elevated-temperature preservation and the dissolution into the electrolytic solution of Mn, and the problem about a cycle property have been still more nearly unsolved.
[0010] Moreover, although it is abundant in [Mn] resources, and it will be thought that it is very useful if the positive-electrode material which carried out the low Fe at the base for [Mn / Co, nickel,] whether being ** also about toxicity is realizable, property sufficient in an old examination is not acquired. Until now, it is $LiCoO_2$. $LiNiO_2$ $LiFeO_2$ which has similar structure Although examination of material considered as basic composition has been carried out to the center, structure is unstable and only the inadequate property is completely realized as a positive active material for rechargeable batteries in the top where production is difficult.

[0011] On the other hand, also about the electrolytic solution, conventionally, the inflammable organic solvent is used and it has left various problems. For example, a high current flows and generates heat rapidly at the time of an unprepared short circuit, the electrolytic solution causes evaporation and decomposition by this, and there is a problem of generating gas. Generating of such gas may lead to breakage, destruction, etc. of a cell.

[0012] Management of preparing the relief valve and current interrupting device which cleave by elevation of cell internal pressure as the solution method is made.

[0013] However, in improvement of such a structure and a mechanism, it does not restrict that any problems can be coped with, but a radical improvement of cell material is needed.

[0014] Then, this invention aims at offering the nonaqueous electrolyte cell which can reduce the problem of environmental correspondence nature or safety, being proposed in view of this conventional actual condition, and realizing high-capacity-izing and low-cost-ization.

[0015]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention is [occlusion, the negative electrode to emit, and] a general formula LixMyPO4 (however, 0<=x<=2 and y of x are 0.8<=y<=1.2 among a formula.) in reversible about a lithium. Moreover, M is a component containing 3d transition metals. It has a positive electrode containing the compound expressed, and an electrolyte, and the above-mentioned electrolyte is characterized by containing a siloxane derivative.

[0016] Fe is abundant for whether it being ** in resources compared with elements, such as Co, nickel, and Mn, and its price is also cheap, and it is nonpoisonous so that it may be known well -- it is harmless Furthermore, Si which is the principal component of a siloxane derivative, and existing very abundantly on the earth are also known well.

[0017] therefore, LiFePO4 from -- by combining the becoming positive-electrode material and the electrolyte containing a siloxane derivative, a low electrochemistry device is extremely realized for an environmental load or toxicity by the low cost

[0018] Furthermore, chemical stability is high, by using for electrolyte material the siloxane which is the inorganic polymer of fire-resistant and low vapor pressure, evaporation of the electrolytic solution and decomposition are suppressed, breakage of a cell and the danger of ignition are also suppressed simultaneously, and the outstanding cell performance is attained.

[0019] In addition, LiFePO4 Since covalent bond of the oxygen is firmly carried out to P, maceration cannot happen very easily and it has the feature of being hard to carry out induction of the combustion reaction. Therefore, the property of the fire retardancy and low vapor pressure which the above-mentioned siloxane derivative has, and a cell system with safety high conjointly very are built.

[0020]

[Embodiments of the Invention] Hereafter, the composition of the nonaqueous electrolyte cell which applied this invention is explained in detail, referring to a drawing.

[0021] The nonaqueous electrolyte cell of this invention is equipped with a positive electrode, a negative electrode, and an electrolyte as a fundamental component.

[0022] (And the compound LixMyPO4 (however, 0<=x<=2 and y of x are 0.8<=y<=1.2 among a formula.) which has olivine structure as a positive active material first in this invention, i.e., a general formula) Moreover, M is a component containing 3d transition metals. The compound expressed is used.

[0023] As a compound expressed with LixMyPO4, LixFeyPO4, LixMnyPO4, LixCoyPO4, LixNiyPO4, LixCuyPO4, Lix(Fe, Mn) yPO4, Lix(Fe, Co) yPO4, Lix(Fe, nickel) yPO4, Lix(Cu, Mn) yPO4, Lix(Cu, Co) yPO4, and Lix(Cu, nickel) yPO4 grade are mentioned, for example. In addition, in each compound, the composition ratio of the element in a parenthesis is arbitrary.

[0024] For example, LiFePO4 Volume density is 3.6 g/cm3. It is large, and the high potential of 3.4V is generated and geometric capacity is also as large as 170 mAh/g. And LiFePO4 It is an initial state, and electrochemically, since one Li in which a ** dope is possible is included per Fe atom, capacity is very high as a positive active material of a lithium ion battery. Moreover, it is this LiFePO4 so that it may mention later. It is compoundable by the simple method.

[0025] however, the above LiFePO4 LiFePO4 obtained by the old synthesis method when it is going

to use as a positive active material of an actual cell **** -- only about [60 mAh/g-70 mAh/g] actual capacity is obtained, but actual capacity of about 120 mAh/g is realized at the maximum -- it is not alike too much Considering that geometric capacity is 170 mAh/g, it is hard to say that sufficient capacity is attained.

[0026] for example, LiFePO4 the case where LiMn 2O4 is compared -- LiMn 2O4 -- average voltage -- 3.9V -- it is -- the capacity of 120 mAh/g -- having -- further -- volume density -- 4.2g/cm3 it is -- since -- LiFePO4 As compared with LiMn 2O4, voltage and volume density will be small about ten percent. For this reason, LiFePO4 which has the capacity of the same 120 mAh/g It will become small twenty percent or more with a volume energy density ten percent or more with a weight energy density rather than LiMn 2O4.

[0027] Therefore, LiFePO4 It is LiFePO4 although 140 mAh/g or the capacity beyond it is required in order to realize LiMn 2O4, equivalent level, or the energy density beyond it. Such high capacity is not realized until now.

[0028] Moreover, LiFePO4 It is conventionally compounded by [of 800 degrees C] being comparatively heated at an elevated temperature under reduction environment using the salt of the divalent iron of iron acetate Fe(CH3COO)2 grade as a source of Fe used as a synthetic powder. When the heating temperature at the time of composition is high, the load which will consume the part energy and is given to a reactor etc. is also large.

[0029] Furthermore, LiFePO4 compounded by [of 800 degrees C] being comparatively heated at an elevated temperature Crystallization will advance superfluously. For this reason, it is LiFePO4 when it uses for the positive active material of a nonaqueous electrolyte cell. Diffusion of the lithium within a particle does not fully take place, but there is a possibility that a capacity high enough cannot be obtained.

[0030] That these problems should be solved, as a result of repeating various examination, it is LixMyPO4. If carried out, it turns out that it is good to use the thing containing that whose particle diameter is 10 micrometers or less. LixMyPO4 which a positive active material contains LixMyPO4 whose particle diameter it carries out and is 10 micrometers or less Since particle size distribution are not suitable when it does not contain, what the lithium which is a charge carrier cannot fully diffuse in the particle of a positive active material is conjectured.

[0031] Moreover, LixMyPO4 It is desirable that the diameter of 10% volume accumulation is 1 micrometer or less. It is LixMyPO4 when the diameter of 10% volume accumulation is larger than 1 micrometer. There is a possibility that crystallization may advance too much and a giant particle may occupy most. Thus, when crystallization advances too much, there is a possibility that the lithium which is a charge carrier cannot be smoothly spread in the particle of a positive active material.

[0032] LixMyPO44 which has the above particle size distributions, for example, LiFePO, Below, as it is shown below, it compounds.

[0033] First, iron acetate (Fe2 (CH3COO)), phosphoric-acid hydrogen ammonium (NH4H2PO4), and a lithium carbonate (Li2CO3) are mixed by the predetermined ratio as a synthetic powder, and it considers as a precursor. Here, mixture of a synthetic powder is fully performed. Since each raw material is mixed uniformly and a point of contact increases by fully mixing a synthetic powder, it is LiFePO4 at low temperature from the former. It becomes possible to compound.

[0034] Next, it is LiFePO4 by heating this precursor at predetermined temperature among inert gas atmosphere, such as nitrogen. It is compounded.

[0035] The former and LiFePO4 For example, it was compounded at the comparison-elevated temperature of 800 degrees C. When the temperature at the time of composition was high, the load which will consume the part energy and is given to a reactor etc. was also large.

[0036] Then, by fully mixing a synthetic powder, considering as a precursor, and compounding by heating in a nitrogen air current, it compares with conventional 800 degrees C of 300 degrees C, and is LiFePO4 at low temperature far. It becomes possible to compound. That is, it compares with the former and is LiFePO4 at a latus temperature requirement more. It becomes possible to compound and the width of face of selection of the temperature at the time of composition spreads.

[0037] this invention person is LiFePO4. The temperature (synthetic temperature is called hereafter.) which heats a precursor in case it compounds, and LiFePO4 The synthetic temperature of optimal

LiFePO4 was examined paying attention to the relation with the capacity of the cell used as an active material.

[0038] Consequently, LiFePO4 Synthetic temperature was understood that it is desirable to consider as the range of 400 degrees C or more and 700 degrees C or less. As for synthetic temperature, it is more desirable that it is the range of 400 degrees C or more and 600 degrees C or less.

[0039] LiFePO4 Crystallization does not fully progress with a low and a chemical reaction rather than 400 degrees C, but synthetic temperature is uniform LiFePO4. It cannot obtain. Moreover, when the synthetic temperature of LiFePO4 is higher than 700 degrees C, crystallization advances superfluously and there is a possibility that a deposit of an impurity may not be suppressed.

[0040] In addition, in the manufacture method mentioned above, before carrying out heating composition of the precursor, it is desirable to remove beforehand the air which performs deairation processing to a precursor and is contained in a precursor.

[0041] It is LiFePO4 when air remains in a precursor. At the time of composition, Fe2+ in the iron acetate which is a divalent iron compound will oxidize by the oxygen in air, and will turn into Fe3+. Consequently, the trivalent iron compound which is an impurity is LiFePO4 of a product. It will mix in inside. By removing the air beforehand contained by deairation processing in a precursor, oxidization of Fe2+ in iron acetate can be prevented. Consequently, a trivalent iron compound is LiFePO4 of a product. It does not mix in inside but is LiFePO4 of single phase. It can obtain.

[0042] LiFePO4 Although various raw materials, such as a lithium hydroxide, a lithium nitrate, an acetic-acid lithium, a phosphoric-acid lithium, the first iron of a phosphoric acid, and a ferrous oxide, can be used as a synthetic powder besides the compound mentioned above, in order [which is called 400 degrees C or more and 700 degrees C or less] to compound at low temperature comparatively, it is desirable to use a reactant high raw material.

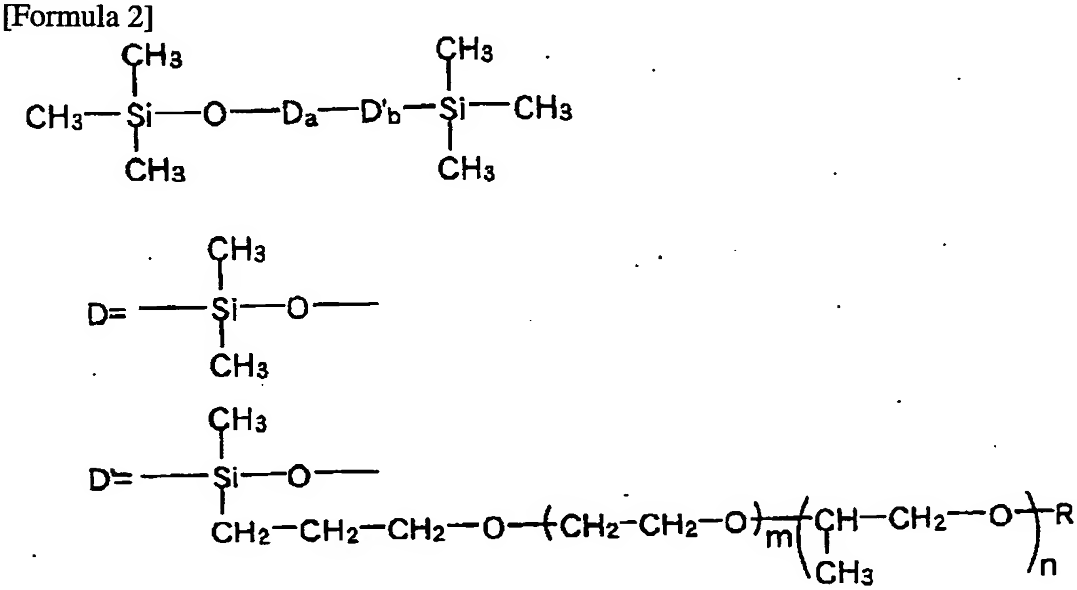
[0043] By the manufacture method which was mentioned above, since a synthetic powder is mixed, it considers as a precursor and this precursor is heated at the temperature of 400 degrees C or more and 700 degrees C or less, a chemical reaction and crystallization advance uniformly and crystallization does not advance too much. Thereby, there is no impurity and it is LiFePO4 of single phase. It is obtained. Thus, LiFePO4 compounded It will be LiFePO4 if it uses as a positive active material. The high actual capacity for which 170 mAh/g which is geometric capacity is pressed is realizable.

[0044] in addition, LiFePO4 which mentioned the above-mentioned manufacture method above not only -- general formula LixMyPO4 It is applied also to the compound expressed.

[0045] On the other hand, in this invention, the siloxane derivative in which an electrolyte is shown by following ** 2 is contained.

[0046]

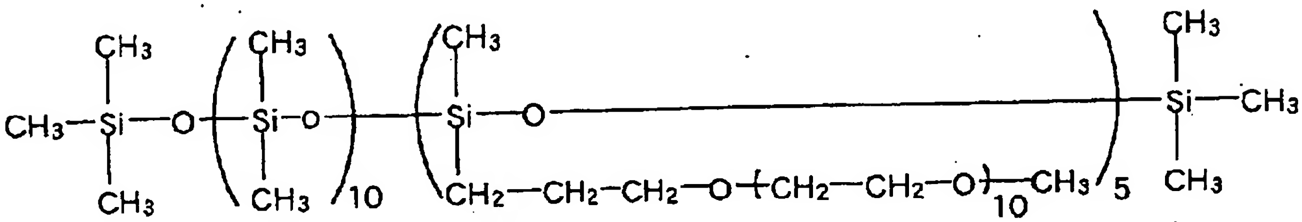
[Formula 2]



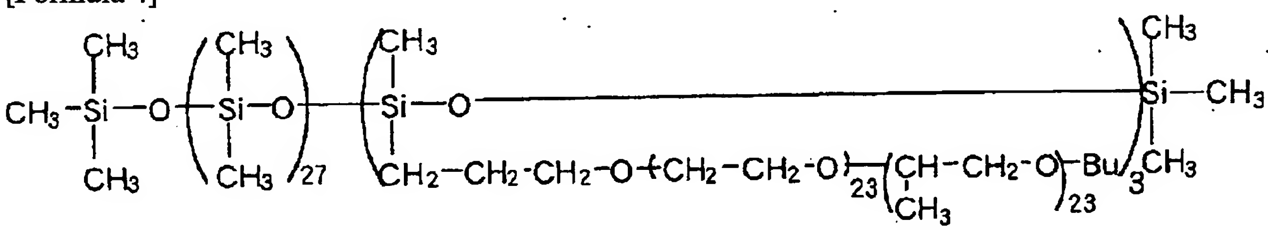
（式中、aは０から１００の整数を表し、bは１から１００の整数を表し、m

は0から100の整数を表し、nは0から100の整数を表し、Rは水素原子又はアルキル基を表す。ただし、b＞1のときは、b個のD′は同じでも異なっていてもよい。D′及びRに含まれる水素原子はハロゲン原子で置き換えられていてもよい。)

[0047] The siloxane derivative which specifically has structure as shown in following ** 3 --izing 5 can be used.
[0048]
[Formula 3]

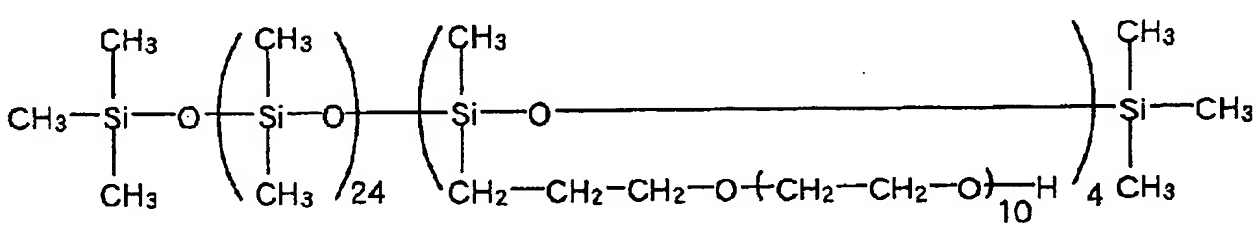


[0049]
[Formula 4]



($Bu= —CH_2—CH_2—CH_2—CH_3$)

[0050]
[Formula 5]



[0051] It is the shape type siloxane derivative of a chain with which it had the chain combination of a silicon and oxygen in the basic skeleton, and the univalent organic machine was added to the silicon as a side chain, its chemical stability is high, and since the above-mentioned siloxane derivative is low vapor pressure in fire retardancy, it is an inorganic polymer which is excellent also in thermochemical stability.
[0052] An electrolyte may be the so-called liquefied electrolytic solution, and may be a solid electrolyte and a gel electrolyte.
[0053] When making an electrolyte into the electrolytic solution, viscosity is a low solution-like comparatively, and a siloxane derivative is asked for the structure where a light metal salt may be

dissolved. That is, coefficients of kinematic viscosity [in / the temperature of 25 degrees C / in a siloxane derivative] are below 5000cSt(s) (centistokes), and it is called for that average molecular weight is 10000 or less.

[0054] Furthermore, it is more desirable that the conductivity in the temperature of 25 degrees C is - one or more 0.1 mS-cm as the electrolytic solution.

[0055] The proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture become possible by choosing moderately the side chain of the monomer unit D in the siloxane derivative shown by ** 2, and D'. As for especially the side chain of monomer unit D', it is advantageous to include ether linkage. Moreover, the hydrogen in D, D', and Substituent R may be replaced by halogens, such as a fluorine and boron.

[0056] As a non-aqueous solvent of the electrolytic solution, propylene carbonate, ethylene carbonate, butylene carbonate, vinylene carbonate, gamma-butyrolactone, a sulfolane, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, 2-methyl tetrahydrofuran, the 3-methyl 1, 3-dioxolane, a methyl propionate, a methyl butyrate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, etc. can be used, for example. It is desirable to use chain-like carbonate, such as annular carbonate, such as propylene carbonate and vinylene carbonate, dimethyl carbonate, diethyl carbonate, and dipropyl carbonate, from the point of voltage stability especially. Moreover, such a non-aqueous solvent may be used independently, two or more kinds may be mixed and one kind may be used for it.

[0057] Solid electrolyte (the perfect solid electrolyte which does not contain a solvent at all is included.) As polymeric materials to be used, silicon gel, acrylic gel, acrylonitrile gel, As fluorine system polymer, such as poly force FAZEN conversion polymer, a polyethylene oxide, polypropylene oxide and these compound polymer, and a crosslinked polymer, conversion polymer For example, poly (vinylidene full aurora id) and poly (vinylidene full aurora id-co-hexafluoropropylene), Although such mixture can carry out various use of poly (vinylidene full aurora id-co-tetrafluoroethylene), poly (vinylidene full aurora id-co-truffe RUORO ethylene), etc., of course, it is not limited to these.

[0058] Moreover, it is good also considering the constituent which consists of two or more sorts of high molecular compounds which can form both the half-invasion type macromolecule network structure mutually as matrix polymer of a solid electrolyte or a gel electrolyte.

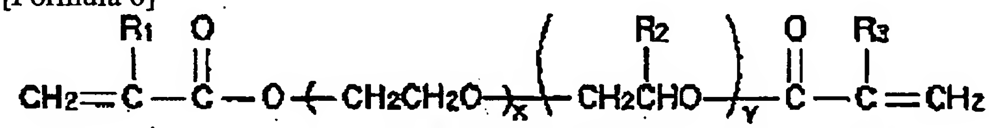
[0059] Among these, it is the 1st high molecular compound with which the bridge was constructed over the compound with which at least one sort of high molecular compounds have chemically the functional group which can construct a bridge in the point concerned constructing a bridge, and at least one sort of other high molecular compounds are the 2nd high molecular compound which does not have the functional group which can construct a bridge but dissolves a light metal salt, i.e., the above-mentioned siloxane derivative.

[0060] The siloxane derivative which is the 2nd high molecular compound will be compatible [in the basic skeleton of the 3-dimensional network structure of the 1st high molecular compound] of this constituent.

[0061] Generally, since the bridge is constructed over the 1st high molecular compound, although a mechanical strength is strong, a molecular motion is suppressed by bridge formation, dissolved mobility of ion becomes small, and it has the property in which ionic conductivity is small. On the other hand, since a bridge is not constructed over the 2nd high molecular compound, although its momentum of a molecule is high, and its glass transition temperature is also low and it has high ionic conductivity, it has the property to be inferior to a mechanical strength.

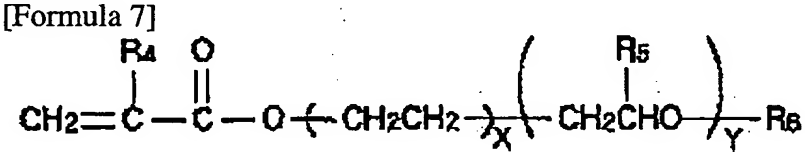
[0062] Here, the 1st high molecular compound and 2nd high molecular compound form both the half-invasion type macromolecule network structure, and those advantages (a strong mechanical strength and high ion conductivity) are employed efficiently, respectively. That is, in both the half-invasion type macromolecule network structure, between the 1st high molecular compound and the 2nd high molecular compound, a chemical bond does not arise substantially and the molecular motion of the 2nd high molecular compound is not suppressed. Moreover, the synergistic effect that crystallization of the 2nd high molecular compound stops being able to happen easily is also added, and ion conductivity higher than a case high-molecular-compound independent [each] is obtained by the latus temperature requirement. Furthermore, a strong mechanical strength is obtained according to the 3-dimensional network structure which the 1st high molecular compound constitutes.

[0063] As the 3-dimensional network structure by bridge formation, what constructed the bridge in the both ends of a straight chain-like compound or the compound of the letter of branching and the piece end, the thing which constructed the bridge in the compound which has a point constructing a bridge in a side chain are arbitrary.
[0064] However, in the above-mentioned 3-dimensional network structure, in order to realize higher ionic conductivity, it is desirable to have the free end side chain including ether linkage like the branching structure of polyoxyalkylene.
[0065] As the structure of cross linkage of the 1st high molecular compound, although ether linkage, ester combination, a urethane bond, etc. are mentioned, of course not only according to this but a use etc., the arbitrary structure of cross linkage is employable.
[0066] The polymer of the diester compound shown in following ** 6 as an example of such 1st high molecular compound can be mentioned.
[0067]
[Formula 6]



（式中、R_1，R_2およびR_3は水素原子または炭素数１～６のアルキル基を示し、それぞれは同一であっても異なっていてもよい。また、ｘ≧１かつｙ≧０またはｘ≧０かつｙ≧１である。）

[0068] In this case, it is desirable to use together the monoester compound shown in following ** 7 for the purpose of introducing a free end side chain which was mentioned above.
[0069]
[Formula 7]



（式中、R_4，R_5およびR_6は水素原子または炭素数１～６のアルキル基を示し、それぞれは同一であっても異なっていてもよい。また、Ｘ≧１かつＹ≧０またはＸ≧０かつＹ≧１である。）

[0070] As for the ratio (a monoester compound / diester compound) of the diester compound at that time, and a monoester compound, it is desirable to carry out to 5.0 or less by the weight ratio.
[0071] The salt of light metals, such as a lithium, sodium, and aluminum, can be used for the light metal salt dissolved in the above-mentioned electrolyte (compatibility), and it can set to it expedient according to the kind of cell.
[0072] for example, in constituting a lithium or a rechargeable lithium-ion battery LiBF4, LiClO4, LiPF6, LiAsF6, CF3SO3Li, 2NLi, C4F9SO3Li, CF3CO2Li, (CF3SO2) 2NLi, C6F5SO3Li, C8F17SO3Li, (CF3CO2) It NLi(s) and NLi(s) (CF(C4F9SO2)3SO2). (C2F5SO2) 2 -- (FSO2C6F4) NLi, 2(2(CF3) CHOSO2) NLi, 3(CF3SO2) CLi, and 4 (3 C6F3(CF3)2- 5) -- the lithium salt of BLi, LiCF3, and LiAlCl4 grade can be used (CF3SO2)
[0073] Although a nonaqueous electrolyte cell is equipped with components, such as a negative electrode besides the above-mentioned positive electrode and an electrolyte, other components can use the conventional thing and the same thing.
[0074] Hereafter, a button type cell is made into an example and the component of a nonaqueous electrolyte cell is explained.
[0075] In equipping the button type nonaqueous electrolyte cell 1 with the separator 6 allotted between the positive-electrode can 5 which holds a negative electrode 2, the negative-electrode can 3 which holds a negative electrode 2, a positive electrode 4, and a positive electrode 4 as shown in drawing 1 , and a positive electrode 4 and a negative electrode 2, and an insulating gasket 7 and using the electrolytic solution as an electrolyte, it comes to fill up nonaqueous electrolyte in the negative-

electrode can 3 and the positive-electrode can 5. In using a solid electrolyte and a gel electrolyte, it forms a solid electrolyte layer and a gel electrolyte layer on the active material layer of a negative electrode 2 or a positive electrode 4.
[0076] It comes to form the negative-electrode active material layer to which a negative electrode 2 contains a negative-electrode active material on a negative-electrode charge collector. As a negative-electrode charge collector, a nickel foil etc. is used, for example.
[0077] As a negative-electrode active material, a conductive polymer, stratified compounds, etc. (carbon-material metallurgy group oxide etc.) with which the metal lithium, the lithium alloy, and the lithium were specifically doped using the thing in which a dope / ** dope is possible in the lithium are used.
[0078] As a binder contained in a negative-electrode active material layer, a well-known resin material usually used as a binder of the negative-electrode active material layer of this kind of nonaqueous electrolyte cell can be used. When for example, a metal lithium foil is used as a negative-electrode active material, the above-mentioned binder is unnecessary.
[0079] The negative-electrode can 3 holds a negative electrode 2, and serves as an external terminal (negative electrode) of the nonaqueous electrolyte cell 1.
[0080] It comes to form the positive-active-material layer which contains LixMyPO4 (for example, LiFePO4) which explained the positive electrode 4 previously on the positive-electrode charge collector as a positive active material.
[0081] As a positive-electrode charge collector, an aluminum foil etc. is used, for example.
[0082] As a binder contained in a positive-active-material layer, a well-known resin material usually used as a binder of the positive-active-material layer of this kind of nonaqueous electrolyte cell can be used.
[0083] The positive-electrode can 5 holds a positive electrode 4, and serves as an external terminal (positive electrode) of the nonaqueous electrolyte cell 1 too.
[0084] Separator 6 can make a positive electrode 4 and a negative electrode 2 able to estrange, and a well-known material usually used as separator of this kind of nonaqueous electrolyte cell can be used, for example, high polymer films, such as polypropylene, are used. Moreover, the thickness of the relation between lithium ion conductivity and an energy density to separator needs a thing thin as much as possible. Specifically, the thickness of separator has desirable 50 micrometers or less. In addition, when a solid electrolyte and a gel electrolyte are used as an electrolyte, it is not necessary to necessarily form this separator 6.
[0085] The insulating gasket 7 is incorporated and united with the negative-electrode can 3. This insulating gasket 7 is for preventing exsorption of the nonaqueous electrolyte with which it filled up in the negative-electrode can 3 and the positive-electrode can 5.
[0086] The nonaqueous electrolyte cell concerning this invention may be a primary cell, and may be a rechargeable battery. Moreover, it is not limited especially about the configuration and let cylindrical, a square shape, a coin type, a button type, etc. be a thin shape, large-sized **, and arbitrary sizes.
[0087]
[Example] Hereafter, the nonaqueous electrolyte cell of this invention is explained based on a concrete experimental result.
[0088] Here, it is olivine type LiFePO4. The nonaqueous electrolyte rechargeable battery made into a positive active material was produced.
[0089] LiFePO4 In order to have compounded, the phosphoric-acid 2 hydrogen ammonium (NH4H2PO4) of a raw material with large microcrystal size was fully ground beforehand first. Next, it fully mixed and iron acetate (Fe2 (CH3COO)), phosphoric-acid 2 hydrogen ammonium (NH4H2PO4), and the lithium carbonate (Li2CO3) were used as the precursor so that a mole ratio might be set to 2:2:1.
[0090] Next, it is LiFePO4 by heating a precursor at 550 degrees C under nitrogen-gas-atmosphere mind for 24 hours, after performing temporary baking of 12 hours for a precursor at 320 degrees C under nitrogen-gas-atmosphere mind. It compounded.
[0091] LiFePO4 compounded by method which was mentioned above ******** -- the powder X diffraction pattern was measured The measurement conditions of a powder X diffraction are as

follows.
[0092]
used equipment: -- Rigaku RINT2500 rotating-target X-ray: -- 40kV of CuKalpha, the slit width:diver Gent (slit DS) =1 degree RESHIBINGU (slit RS) =1 degree (scattering slit SS) =1.5mm counter:scintillation counter measuring method:reflection methods of which a vertical-mold standard and 100mA goniometer:radius counter monochromator [of 185mm]:use filter:use are not done, and the powder X-ray patterns measured by continuation scan scanning-zone:2 theta= 10 degrees - 80 degree scan speed:4 degree Compounded LiFePO4 It sets and is LiFePO4 in a product. It is not checked but existence of the impurity of an except is LiFePO4 of single phase. It turns out that it is obtained.
[0093] LiFePO4 which is there, next was obtained as mentioned above It used as a positive active material and the cell was produced.
[0094] first, 70 % of the weight (dry LiFePO4) of positive active materials and an electric conduction agent (acetylene black) -- 25 % of the weight and 5 % of the weight (polyvinylidene fluoride) of binders -- ****(ing) -- this -- the inside of a solvent (dimethylformamide) -- supplying -- uniform -- mixing -- a paste-like positive electrode -- the mixture was prepared In addition, Aldrich 1300 [#] were used for the polyvinylidene fluoride.
[0095] next, this positive electrode -- the mixture was applied on the aluminum mesh used as a charge collector, under dryness argon atmosphere, it dried at 100 degrees C for 1 hour, and the positive-active-material layer was formed
[0096] And the aluminum mesh in which the positive-active-material layer was formed was made into the pellet-like positive electrode by piercing to disc-like [with a diameter of 15mm]. In addition, the 60mg active material is supported by this one positive electrode.
[0097] Next, it considered as the negative electrode by piercing a lithium metallic foil to a positive electrode and abbreviation isomorphism.
[0098] Subsequently, nonaqueous electrolyte was prepared by dissolving one-mol LiN (CF3SO2)2 to siloxane 1kg.
[0099] The positive electrode obtained as mentioned above was held in the positive-electrode can, the negative electrode was held in the negative-electrode can, and separator was allotted between the positive electrode and the negative electrode. Nonaqueous electrolyte was poured in into the positive-electrode can and the negative-electrode can, and the 2025 type coin type test cell was produced by fixing a positive-electrode can and a negative-electrode can in total.
[0100] The charge and discharge test was performed about this test cell. After performing constant-current charge to 4.0V to a test cell, electric discharge was performed and the time of a cell voltage falling to 2.5V was considered as the electric discharge end. In addition, charge and electric discharge are performed in ordinary temperature (23 degrees C), and, for charge and electric discharge, current density is 0.12 mA/cm2. It carried out.
[0101] A charge-and-discharge property is shown in drawing 3 . Drawing 3 shows that the test cell of this example has a good charge-and-discharge property.
[0102]
[Effect of the Invention] According to this invention, the nonaqueous electrolyte cell which was excellent in a cell property, economical efficiency, environmental correspondence nature, and all the safeties can be realized, and a practical advantage is large so that clearly also from the above explanation.
[0103] Moreover, since voltage is set up lowness rather than the conventional lithium ion battery, the nonaqueous electrolyte cell of this invention can respond also to the fall of driver voltages, such as IC.

[Translation done.]

TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the nonaqueous electrolyte cell which makes the compound which has order type olivine structure a positive active material.

[Translation done.]

PRIOR ART

[Description of the Prior Art] In recent years, research of the rechargeable battery in which a recharge is possible is advanced as a cell which can be used conveniently [for a long time] and economically with fast progress of various electronic equipment. As a typical rechargeable battery, the lead accumulator, the alkaline battery, the lithium secondary battery, etc. are known.
[0003] Also in the above rechargeable batteries, especially the lithium secondary battery has advantages, such as high power and high-energy density. A lithium secondary battery consists of occlusion, the negative electrode and positive electrode which have the active material which can be emitted, and nonaqueous electrolyte in reversible in a lithium ion.
[0004] And generally as a negative-electrode active material of a lithium secondary battery, a conductive polymer, stratified compounds, etc. (carbon-material metallurgy group oxide etc.) with which the metal lithium, the lithium alloy, and the lithium were doped are used.
[0005] moreover, as a positive active material, a metallic oxide, metallic sulfide, or polymer uses -- having -- Ti_2S, MoS_2 and $NbSe_2$, and V_2O_5 etc. -- the non-** lithium compound and the multiple oxide containing Li like Li_xMO_2 (M=Co, nickel, Mn, Fe, etc.) are proposed [for example,]

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, the nonaqueous electrolyte cell which was excellent in a cell property, economical efficiency, environmental correspondence nature, and all the safeties can be realized, and a practical advantage is large so that clearly also from the above explanation.
[0103] Moreover, since voltage is set up lowness rather than the conventional lithium ion battery, the nonaqueous electrolyte cell of this invention can respond also to the fall of driver voltages, such as IC.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] By the way, in the above-mentioned lithium secondary battery, various technical problems are left behind and those improvements are demanded.
[0007] For example, LiCoO2 which has the potential of pair Li4V from a viewpoint that high-energy density and the high voltage are obtained in the conventional lithium secondary battery It is widely put in practical use as a positive electrode. LiCoO2 In respect of being various, although it is an ideal positive-electrode material, Co is unevenly distributed as resources on the earth, and since it is rare, it requires great cost, and it has the problem that a problem is in adequate supply, and development of the positive-electrode material replaced with this is desired.
[0008] In the present condition, LiMn 2O4 (space group Fd3m) which has normal-spinel type structure is the positive-electrode material of the 4V class only Mn base, from the point of the easy synthesis method and cell capacity, is very promising and is already put in practical use in part.
[0009] However, when the application to a real cell is considered, it is left behind while the problem about stability, such as capacity degradation at the time of elevated-temperature preservation and the dissolution into the electrolytic solution of Mn, and the problem about a cycle property have been still more nearly unsolved.
[0010] Moreover, although it is abundant in [Mn] resources, and it will be thought that it is very useful if the positive-electrode material which used Fe lower than Co, nickel, Mn, etc. for whether it being ** as the base also about toxicity is realizable, property sufficient in an old examination is not acquired. Until now, it is LiCoO2. LiNiO2 LiFeO2 which has similar structure Although examination of material considered as basic composition has been carried out to the center, structure is unstable and only the inadequate property is completely realized as a positive active material for rechargeable batteries in the top where production is difficult.
[0011] On the other hand, also about the electrolytic solution, conventionally, the inflammable organic solvent is used and it has left various problems. For example, a high current flows and generates heat rapidly at the time of an unprepared short circuit, the electrolytic solution causes evaporation and decomposition by this, and there is a problem of generating gas. Generating of such gas may lead to breakage, destruction, etc. of a cell.
[0012] Management of preparing the relief valve and current interrupting device which cleave by the rise of cell internal pressure as the solution method is made.
[0013] However, in improvement of such a structure and a mechanism, it does not restrict that any problems can be coped with, but a radical improvement of cell material is needed.
[0014] Then, this invention aims at offering the nonaqueous electrolyte cell which can reduce the problem of environmental correspondence nature or safety, being proposed in view of this conventional actual condition, and realizing high-capacity-izing and low-cost-ization.

[Translation done.]

MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention is [occlusion, the negative electrode to emit, and] a general formula LixMyPO4 (however, 0<=x<=2 and y of x are 0.8<=y<=1.2 among a formula.) in reversible about a lithium. Moreover, M is a component containing 3d transition metals. It has a positive electrode containing the compound expressed, and an electrolyte, and the above-mentioned electrolyte is characterized by containing a siloxane derivative.

[0016] Fe is abundant for whether it being ** in resources compared with elements, such as Co, nickel, and Mn, and its price is also cheap, and it is nonpoisonous so that it may be known well -- it is harmless Furthermore, Si which is the principal component of a siloxane derivative, and existing very abundantly on the earth are also known well.

[0017] therefore, LiFePO4 from -- by combining the becoming positive-electrode material and the electrolyte containing a siloxane derivative, a low electrochemistry device is extremely realized for an environmental load or toxicity by the low cost

[0018] Furthermore, chemical stability is high, by using for electrolyte material the siloxane which is the inorganic polymer of fire-resistant and low vapor pressure, evaporation of the electrolytic solution and decomposition are suppressed, breakage of a cell and the danger of ignition are also suppressed simultaneously, and the outstanding cell performance is attained.

[0019] In addition, LiFePO4 Since covalent bond of the oxygen is firmly carried out to P, maceration cannot happen very easily and it has the feature of being hard to carry out induction of the combustion reaction. Therefore, the property of the fire retardancy and low vapor pressure which the above-mentioned siloxane derivative has, and a cell system with safety high conjointly very are built.

[0020]

[Embodiments of the Invention] Hereafter, the composition of the nonaqueous electrolyte cell which applied this invention is explained in detail, referring to a drawing.

[0021] The nonaqueous electrolyte cell of this invention is equipped with a positive electrode, a negative electrode, and an electrolyte as a fundamental component.

[0022] (And the compound LixMyPO4 (however, 0<=x<=2 and y of x are 0.8<=y<=1.2 among a formula.) which has olivine structure as a positive active material first in this invention, i.e., a general formula) Moreover, M is a component containing 3d transition metals. The compound expressed is used.

[0023] As a compound expressed with LixMyPO4, LixFeyPO4, LixMnyPO4, LixCoyPO4, LixNiyPO4, LixCuyPO4, Lix(Fe, Mn) yPO4, Lix(Fe, Co) yPO4, Lix(Fe, nickel) yPO4, Lix(Cu, Mn) yPO4, Lix(Cu, Co) yPO4, and Lix(Cu, nickel) yPO4 grade are mentioned, for example. In addition, in each compound, the composition ratio of the element in a parenthesis is arbitrary.

[0024] For example, LiFePO4 Volume density is 3.6 g/cm3. It is large, and the high potential of 3.4V is generated and geometric capacity is also as large as 170 mAh/g. And LiFePO4 It is an initial state, and electrochemically, since one Li in which a ** dope is possible is included per Fe atom, capacity is very high as a positive active material of a lithium ion battery. Moreover, it is this LiFePO4 so that it may mention later. It is compoundable by the simple method.

[0025] however, the above LiFePO4 LiFePO4 obtained by the old synthesis method when it is going to use as a positive active material of an actual cell **** -- only about [60 mAh/g-70 mAh/g] actual capacity is obtained, but actual capacity of about 120 mAh/g is realized at the maximum -- it is not

alike too much Considering that geometric capacity is 170 mAh/g, it is hard to say that sufficient capacity is attained.

[0026] for example, LiFePO4 the case where LiMn 2O4 is compared -- LiMn 2O4 -- average voltage -- 3.9V -- it is -- the capacity of 120 mAh/g -- having -- further -- volume density -- 4.2g/cm3 it is -- since -- LiFePO4 As compared with LiMn 2O4, voltage and volume density will be small about ten percent. For this reason, LiFePO4 which has the capacity of the same 120 mAh/g It will become small twenty percent or more with a volume energy density ten percent or more with a weight energy density rather than LiMn 2O4.

[0027] Therefore, LiFePO4 It is LiFePO4 although 140 mAh/g or the capacity beyond it is required in order to realize LiMn 2O4, equivalent level, or the energy density beyond it. Such high capacity is not realized until now.

[0028] Moreover, LiFePO4 It is conventionally compounded by [of 800 degrees C] being comparatively heated at an elevated temperature under reduction environment using the salt of the divalent iron of iron acetate Fe(CH3COO)2 grade as a source of Fe used as a synthetic powder. When the heating temperature at the time of composition is high, the load which will consume the part energy and is given to a reactor etc. is also large.

[0029] Furthermore, LiFePO4 compounded by [of 800 degrees C] being comparatively heated at an elevated temperature Crystallization will advance superfluously. For this reason, it is LiFePO4 when it uses for the positive active material of a nonaqueous electrolyte cell. Diffusion of the lithium within a particle does not fully take place, but there is a possibility that a capacity high enough cannot be obtained.

[0030] That these problems should be solved, as a result of repeating various examination, it is LixMyPO4. If carried out, it turns out that it is good to use the thing containing,that whose particle diameter is 10 micrometers or less. LixMyPO4 which a positive active material contains LixMyPO4 whose particle diameter it carries out and is 10 micrometers or less Since particle size distribution are not suitable when it does not contain, what the lithium which is a charge carrier cannot fully diffuse in the particle of a positive active material is conjectured.

[0031] Moreover, LixMyPO4 It is desirable that the diameter of 10% volume accumulation is 1 micrometer or less. It is LixMyPO4 when the diameter of 10% volume accumulation is larger than 1 micrometer. There is a possibility that crystallization may advance too much and a giant particle may occupy most. Thus, when crystallization advances too much, there is a possibility that the lithium which is a charge carrier cannot be smoothly spread in the particle of a positive active material.

[0032] LixMyPO44 which has the above particle size distributions, for example, LiFePO, Below, as it is shown below, it compounds.

[0033] First, iron acetate (Fe2 (CH3COO)), phosphoric-acid hydrogen ammonium (NH4H2PO4), and a lithium carbonate (Li2CO3) are mixed by the predetermined ratio as a synthetic powder, and it considers as a precursor. Here, mixture of a synthetic powder is fully performed. Since each raw material is mixed uniformly and a point of contact increases by fully mixing a synthetic powder, it is LiFePO4 at temperature lower than before. It becomes possible to compound.

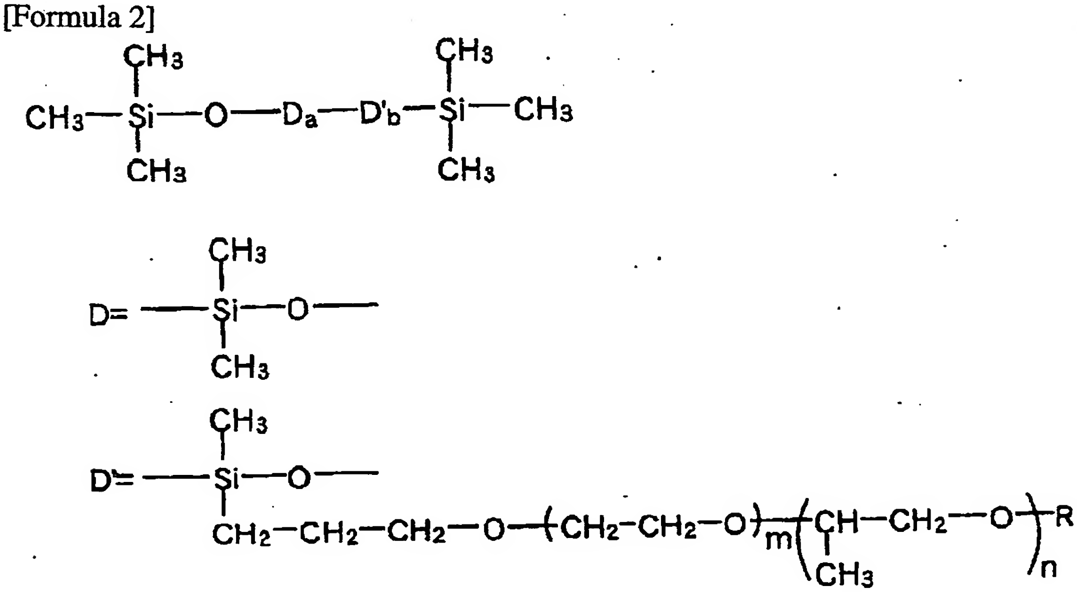
[0034] Next, it is LiFePO4 by heating this precursor at predetermined temperature among inert gas atmosphere, such as nitrogen. It is compounded.

[0035] The former and LiFePO4 For example, it was compounded at the comparison-elevated temperature of 800 degrees C. When the temperature at the time of composition was high, the load which will consume the part energy and is given to a reactor etc. was also large.

[0036] Then, by fully mixing a synthetic powder, considering as a precursor, and compounding by heating in a nitrogen air current, it compares with conventional 800 degrees C of 300 degrees C, and is LiFePO4 at far low temperature. It becomes possible to compound. That is, it compares with the former and is LiFePO4 at a larger temperature requirement. It becomes possible to compound and the width of face of selection of the temperature at the time of composition spreads.

[0037] this invention person is LiFePO4. The temperature (synthetic temperature is called hereafter.) which heats a precursor in case it compounds, and LiFePO4 The synthetic temperature of optimal LiFePO4 was examined paying attention to the relation with the capacity of the cell used as an active material.

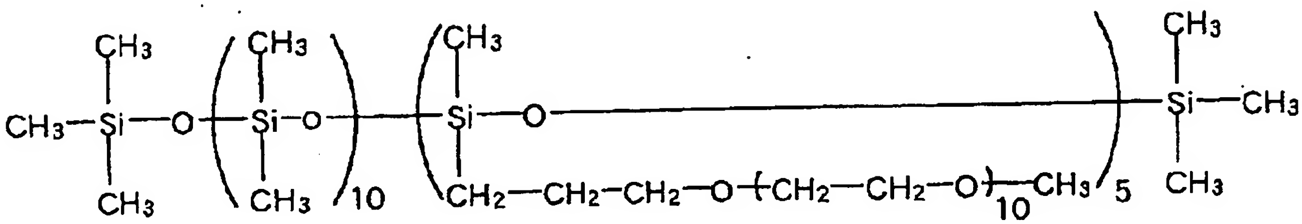
[0038] Consequently, $LiFePO_4$ Synthetic temperature was understood that it is desirable to consider as the range of 400 degrees C or more and 700 degrees C or less. As for synthetic temperature, it is more desirable that it is the range of 400 degrees C or more and 600 degrees C or less.
[0039] $LiFePO_4$ Crystallization does not fully progress with a low and a chemical reaction rather than 400 degrees C, but synthetic temperature is uniform $LiFePO_4$. It cannot obtain. Moreover, when the synthetic temperature of $LiFePO_4$ is higher than 700 degrees C, crystallization advances superfluously and there is a possibility that a deposit of an impurity may not be suppressed.
[0040] In addition, in the manufacture method mentioned above, before carrying out heating composition of the precursor, it is desirable to remove beforehand the air which performs deairation processing to a precursor and is contained in a precursor.
[0041] It is $LiFePO_4$ when air remains in a precursor. At the time of composition, Fe^{2+} in the iron acetate which is a divalent iron compound will oxidize by the oxygen in air, and will turn into Fe^{3+}. Consequently, the trivalent iron compound which is an impurity is $LiFePO_4$ of a product. It will mix in inside. By removing the air beforehand contained by deairation processing in a precursor, oxidization of Fe^{2+} in iron acetate can be prevented. Consequently, a trivalent iron compound is $LiFePO_4$ of a product. It does not mix in inside but is $LiFePO_4$ of single phase. It can obtain.
[0042] $LiFePO_4$ Although various raw materials, such as a lithium hydroxide, a lithium nitrate, an acetic-acid lithium, a phosphoric-acid lithium, the first iron of a phosphoric acid, and a ferrous oxide, can be used as a synthetic powder besides the compound mentioned above, in order [which is called 400 degrees C or more and 700 degrees C or less] to compound at low temperature comparatively, it is desirable to use a reactant high raw material.
[0043] By the manufacture method which was mentioned above, since a synthetic powder is mixed, it considers as a precursor and this precursor is heated at the temperature of 400 degrees C or more and 700 degrees C or less, a chemical reaction and crystallization advance uniformly and crystallization does not advance too much. Thereby, there is no impurity and it is $LiFePO_4$ of single phase. It is obtained. Thus, $LiFePO_4$ compounded It will be $LiFePO_4$ if it uses as a positive active material. The high actual capacity for which 170 mAh/g which is geometric capacity is pressed is realizable.
[0044] in addition, $LiFePO_4$ which mentioned the above-mentioned manufacture method above not only -- general formula $Li_xM_yPO_4$ It is applied also to the compound expressed.
[0045] On the other hand, in this invention, the siloxane derivative in which an electrolyte is shown by following ** 2 is contained.
[0046]
[Formula 2]



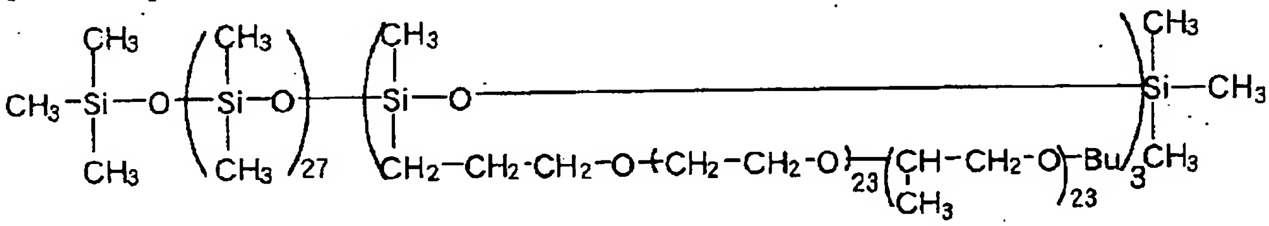
（式中、ａは０から１００の整数を表し、ｂは１から１００の整数を表し、ｍは０から１００の整数を表し、ｎは０から１００の整数を表し、Ｒは水素原子又はアルキル基を表す。ただし、ｂ＞１のときは、ｂ個のＤ′は同じでも

異なっていてもよい。D′及びRに含まれる水素原子はハロゲン原子で置き換えられていてもよい。)

[0047] The siloxane derivative which specifically has structure as shown in following ** 3 --izing 5 can be used.
[0048]
[Formula 3]

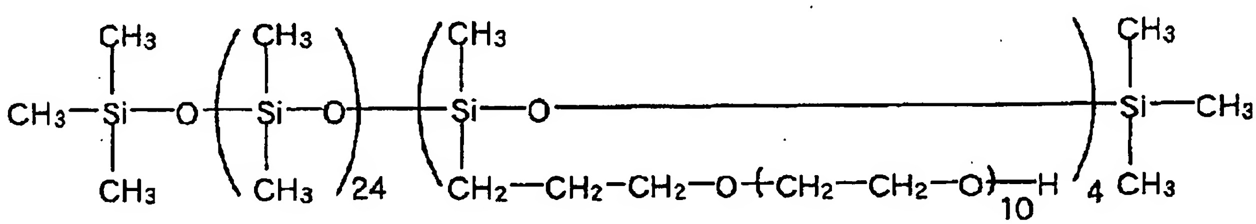


[0049]
[Formula 4]



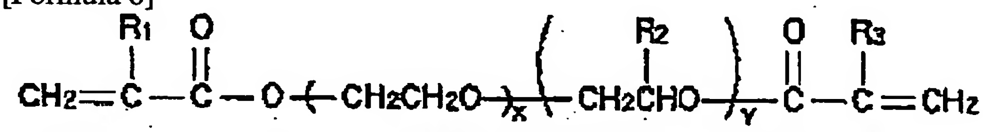
(Bu= —CH2—CH2—CH2—CH3)

[0050]
[Formula 5]



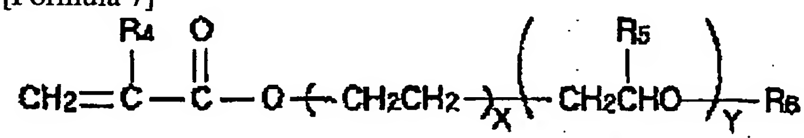
[0051] It is the shape type siloxane derivative of a chain with which it had the chain combination of a silicon and oxygen in the basic skeleton, and the univalent organic machine was added to the silicon as a side chain, its chemical stability is high, and since the above-mentioned siloxane derivative is low vapor pressure in fire retardancy, it is an inorganic polymer which is excellent also in thermochemical stability.
[0052] An electrolyte may be the so-called liquefied electrolytic solution, and may be a solid electrolyte and a gel electrolyte.
[0053] When making an electrolyte into the electrolytic solution, viscosity is a low solution-like comparatively, and a siloxane derivative is asked for the structure where a light metal salt may be dissolved. That is, coefficients of kinematic viscosity [in / the temperature of 25 degrees C / in a siloxane derivative] are below 5000cSt(s) (centistokes), and it is called for that average molecular

piece end, the thing which constructed the bridge in the compound which has a point constructing a bridge in a side chain are arbitrary.
[0064] However, in the above-mentioned 3-dimensional network structure, in order to realize higher ionic conductivity, it is desirable to have the free end side chain including ether linkage like the branching structure of polyoxyalkylene.
[0065] As the structure of cross linkage of the 1st high molecular compound, although ether linkage, ester combination, a urethane bond, etc. are mentioned, of course not only according to this but a use etc., the arbitrary structure of cross linkage is employable.
[0066] The polymer of the diester compound shown in following ** 6 as an example of such 1st high molecular compound can be mentioned.
[0067]
[Formula 6]



（式中、R_1，R_2およびR_3は水素原子または炭素数1～6のアルキル基を
示し、それぞれは同一であっても異なっていてもよい。また、x≧1かつy≧0
またはx≧0かつy≧1である。）

[0068] In this case, it is desirable to use together the monoester compound shown in following ** 7 for the purpose of introducing a free end side chain which was mentioned above.
[0069]
[Formula 7]



（式中、R_4，R_5およびR_6は水素原子または炭素数1～6のアルキル基を
示し、それぞれは同一であっても異なっていてもよい。また、X≧1かつY≧0
またはX≧0かつY≧1である。）

[0070] As for the ratio (a monoester compound / diester compound) of the diester compound at that time, and a monoester compound, it is desirable to carry out to 5.0 or less by the weight ratio.
[0071] The salt of light metals, such as a lithium, sodium, and aluminum, can be used for the light metal salt dissolved in the above-mentioned electrolyte (compatibility), and it can set to it expedient according to the kind of cell.
[0072] for example, in constituting a lithium or a rechargeable lithium-ion battery LiBF4, LiClO4, LiPF6, LiAsF6, CF3SO3Li, 2NLi, C4F9SO3Li, CF3CO2Li, (CF3SO2) 2NLi, C6F5SO3Li, C8F17SO3Li, (CF3CO2) It NLi(s) and NLi(s) (CF(C4F9SO2)3SO2). (C2F5SO2) 2 -- (FSO2C6F4) NLi, 2(2(CF3) CHOSO2) NLi, 3(CF3SO2) CLi, and 4 (3 C6F3(CF3)2- 5) -- the lithium salt of BLi, LiCF3, and LiAlCl4 grade can be used (CF3SO2)
[0073] Although a nonaqueous electrolyte cell is equipped with components, such as a negative electrode besides the above-mentioned positive electrode and an electrolyte, other components can use the conventional thing and the same thing.
[0074] Hereafter, a button type cell is made into an example and the component of a nonaqueous electrolyte cell is explained.
[0075] In equipping the button type nonaqueous electrolyte cell 1 with the separator 6 allotted between the positive-electrode can 5 which holds a negative electrode 2, the negative-electrode can 3 which holds a negative electrode 2, a positive electrode 4, and a positive electrode 4 as shown in drawing 1 , and a positive electrode 4 and a negative electrode 2, and an insulating gasket 7 and using the electrolytic solution as an electrolyte, it comes to fill up nonaqueous electrolyte in the negative-electrode can 3 and the positive-electrode can 5. In using a solid electrolyte and a gel electrolyte, it forms a solid electrolyte layer and a gel electrolyte layer on the active material layer of a negative

electrode 2 or a positive electrode 4.
[0076] It comes to form the negative-electrode active material layer to which a negative electrode 2 contains a negative-electrode active material on a negative-electrode charge collector. As a negative-electrode charge collector, a nickel foil etc. is used, for example.
[0077] As a negative-electrode active material, a conductive polymer, stratified compounds, etc. (carbon-material metallurgy group oxide etc.) with which the metal lithium, the lithium alloy, and the lithium were specifically doped using the thing in which a dope / ** dope is possible in the lithium are used.
[0078] As a binder contained in a negative-electrode active material layer, a well-known resin material usually used as a binder of the negative-electrode active material layer of this kind of nonaqueous electrolyte cell can be used. When for example, a metal lithium foil is used as a negative-electrode active material, the above-mentioned binder is unnecessary.
[0079] The negative-electrode can 3 holds a negative electrode 2, and serves as an external terminal (negative electrode) of the nonaqueous electrolyte cell 1.
[0080] It comes to form the positive-active-material layer which contains LixMyPO4 (for example, LiFePO4) which explained the positive electrode 4 previously on the positive-electrode charge collector as a positive active material.
[0081] As a positive-electrode charge collector, an aluminum foil etc. is used, for example.
[0082] As a binder contained in a positive-active-material layer, a well-known resin material usually used as a binder of the positive-active-material layer of this kind of nonaqueous electrolyte cell can be used.
[0083] The positive-electrode can 5 holds a positive electrode 4, and serves as an external terminal (positive electrode) of the nonaqueous electrolyte cell 1 too.
[0084] Separator 6 can make a positive electrode 4 and a negative electrode 2 able to estrange, and a well-known material usually used as separator of this kind of nonaqueous electrolyte cell can be used, for example, high polymer films, such as polypropylene, are used. Moreover, the thickness of the relation between lithium ion conductivity and an energy density to separator needs a thing thin as much as possible. Specifically, the thickness of separator has desirable 50 micrometers or less. In addition, when a solid electrolyte and a gel electrolyte are used as an electrolyte, it is not necessary to necessarily form this separator 6.
[0085] The insulating gasket 7 is incorporated and united with the negative-electrode can 3. This insulating gasket 7 is for preventing exsorption of the nonaqueous electrolyte with which it filled up in the negative-electrode can 3 and the positive-electrode can 5.
[0086] The nonaqueous electrolyte cell concerning this invention may be a primary cell, and may be a rechargeable battery. Moreover, it is not limited especially about the configuration and let cylindrical, a square shape, a coin type, a button type, etc. be a thin shape, large-sized **, and arbitrary sizes.

[Translation done.]

* NOTICES *

EXAMPLE

[Example] Hereafter, the nonaqueous electrolyte cell of this invention is explained based on a concrete experimental result.
[0088] Here, it is olivine type LiFePO4. The nonaqueous electrolyte rechargeable battery made into a positive active material was produced.
[0089] LiFePO4 In order to have compounded, the phosphoric-acid 2 hydrogen ammonium (NH4H2PO4) of a raw material with large microcrystal size was fully ground beforehand first. Next, it fully mixed and iron acetate (Fe2 (CH3COO)), phosphoric-acid 2 hydrogen ammonium (NH4H2PO4), and the lithium carbonate (Li2CO3) were used as the precursor so that a mole ratio might be set to 2:2:1.
[0090] Next, it is LiFePO4 by heating a precursor at 550 degrees C under nitrogen-gas-atmosphere mind for 24 hours, after performing temporary baking of 12 hours for a precursor at 320 degrees C under nitrogen-gas-atmosphere mind. It compounded.
[0091] LiFePO4 compounded by method which was mentioned above ******** -- the powder X diffraction pattern was measured The measurement conditions of a powder X diffraction are as follows.
[0092]
used equipment: -- Rigaku RINT2500 rotating-target X-ray: -- 40kV of CuKalpha, the slit width:diver Gent (slit DS) =1 degree RESHIBINGU (slit RS) =1 degree (scattering slit SS) =1.5mm counter:scintillation counter measuring method:reflection methods of which a vertical-mold standard and 100mA goniometer:radius counter monochromator [of 185mm]:use filter:use are not done, and the powder X-ray patterns measured by continuation scan scanning-zone:2 theta= 10 degrees - 80 degree scan speed:4 degree Compounded LiFePO4 It sets and is LiFePO4 in a product. It is not checked but existence of the impurity of an except is LiFePO4 of single phase. It turns out that it is obtained.
[0093] LiFePO4 which is there, next was obtained as mentioned above It used as a positive active material and the cell was produced.
[0094] first, 70 % of the weight (dry LiFePO4) of positive active materials and an electric conduction agent (acetylene black) -- 25 % of the weight and 5 % of the weight (polyvinylidene fluoride) of binders -- ****(ing) -- this -- the inside of a solvent (dimethylformamide) -- supplying -- uniform -- mixing -- a paste-like positive electrode -- the mixture was prepared In addition, Aldrich 1300 [#] were used for the polyvinylidene fluoride.
[0095] next, this positive electrode -- the mixture was applied on the aluminum mesh used as a charge collector, under dryness argon atmosphere, it dried at 100 degrees C for 1 hour, and the positive-active-material layer was formed
[0096] And the aluminum mesh in which the positive-active-material layer was formed was made into the pellet-like positive electrode by piercing to disc-like [with a diameter of 15mm]. In addition, the 60mg active material is supported by this one positive electrode.
[0097] Next, it considered as the negative electrode by piercing a lithium metallic foil to a positive electrode and abbreviation isomorphism.
[0098] Subsequently, nonaqueous electrolyte was prepared by dissolving one-mol LiN (CF3SO2)2 to siloxane 1kg.
[0099] The positive electrode obtained as mentioned above was held in the positive-electrode can, the

negative electrode was held in the negative-electrode can, and separator was allotted between the positive electrode and the negative electrode. Nonaqueous electrolyte was poured in into the positive-electrode can and the negative-electrode can, and the 2025 type coin type test cell was produced by fixing a positive-electrode can and a negative-electrode can in total.

[0100] The charge and discharge test was performed about this test cell. After performing constant-current charge to 4.0V to a test cell, electric discharge was performed and the time of a cell voltage falling to 2.5V was considered as the electric discharge end. In addition, charge and electric discharge are performed in ordinary temperature (23 degrees C), and, for charge and electric discharge, current density is 0.12 mA/cm2. It carried out.

[0101] A charge-and-discharge property is shown in drawing 3 . Drawing 3 shows that the test cell of this example has a good charge-and-discharge property.

[Translation done.]

* NOTICES *

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the outline cross section showing the example of 1 composition of a nonaqueous electrolyte cell.
[Drawing 2] Compounded $LiFePO4$ It is drawing showing a powder X diffraction pattern.
[Drawing 3] It is the property view showing the charge-and-discharge property of the produced test cell.

[Translation done.]

* NOTICES *

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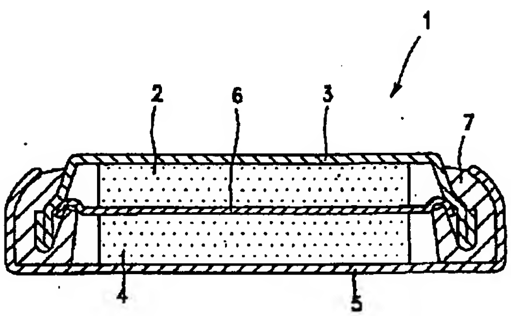
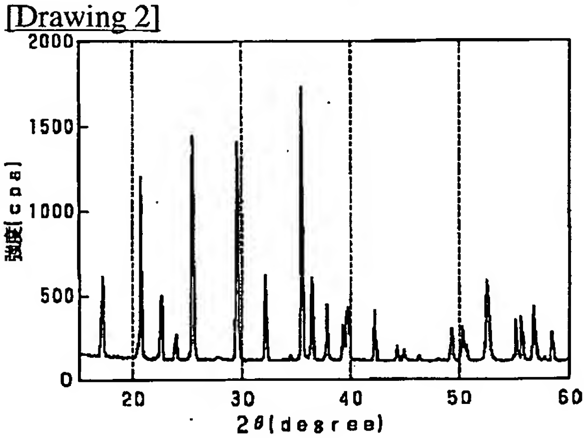
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

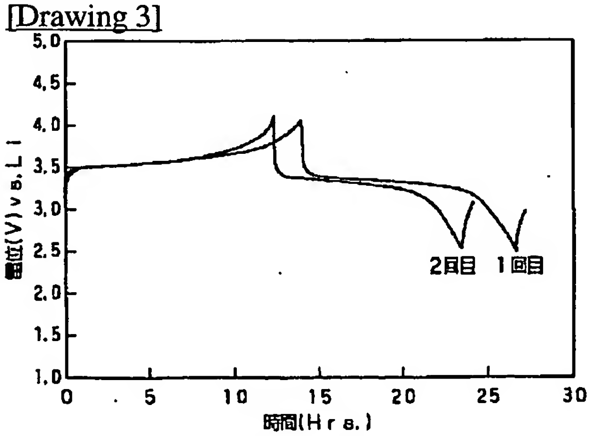
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]